



# **Novel Zeolitic Imidazolate Framework/Polymer Membranes for Hydrogen Separations in Coal Processing**

**Inga H. Musselman, John P. Ferraris, Kenneth J. Balkus, Jr.**

**Department of Chemistry, The University of Texas at Dallas**

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**Program Manager: Dr. Richard Dunst**

**Dr. Inga H. Musselman, Professor**

Ph.D. Analytical Chemistry, U. of North Carolina

[imusselm@utdallas.edu](mailto:imusselm@utdallas.edu)

<http://www.utdallas.edu/chemistry/faculty/musselman.html>

**Dr. John P. Ferraris, Professor**

Ph.D., Organic Chemistry

The Johns Hopkins University

[ferraris@utdallas.edu](mailto:ferraris@utdallas.edu)

[www.utdallas.edu/~ferraris](http://www.utdallas.edu/~ferraris)

**Dr. Kenneth J. Balkus, Jr., Professor**

Ph.D. Inorganic Chemistry, University of Florida

[balkus@utdallas.edu](mailto:balkus@utdallas.edu)

[www.utdallas.edu/~balkus](http://www.utdallas.edu/~balkus)



## I. Introduction

- i. Hydrogen from coal: H<sub>2</sub> separations
- ii. Mixed-matrix membranes (MMMs)

## II. UT-Dallas project

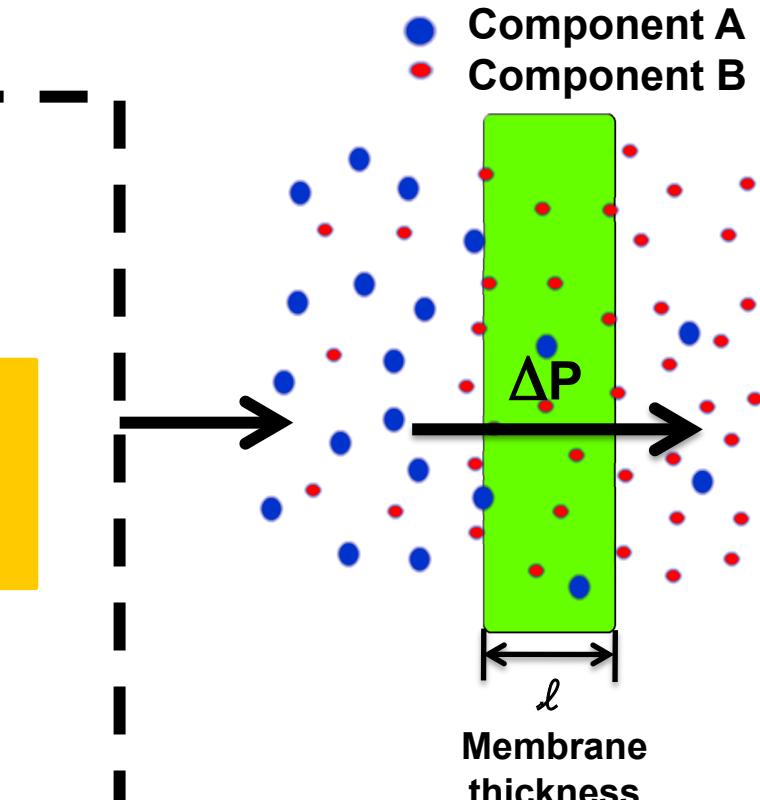
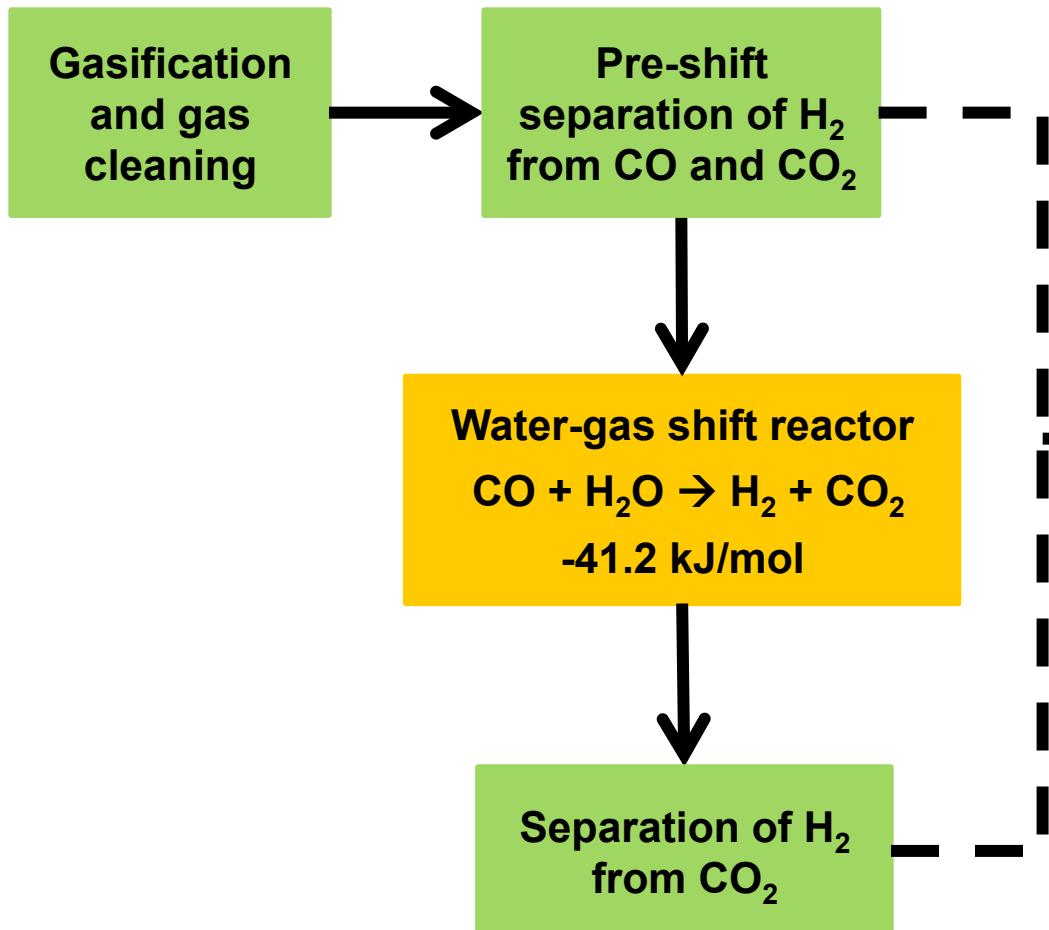
- i. Metal-organic frameworks (MOFs) and zeolitic imidazolate frameworks (ZIFs)
- ii. High performance polymers
- iii. High temperature-high pressure permeameter

## III. Previous results

## IV. New results

## V. Future work

# Coal Gasification



$$\text{Permeability of A} = P_A = S_A D_A$$

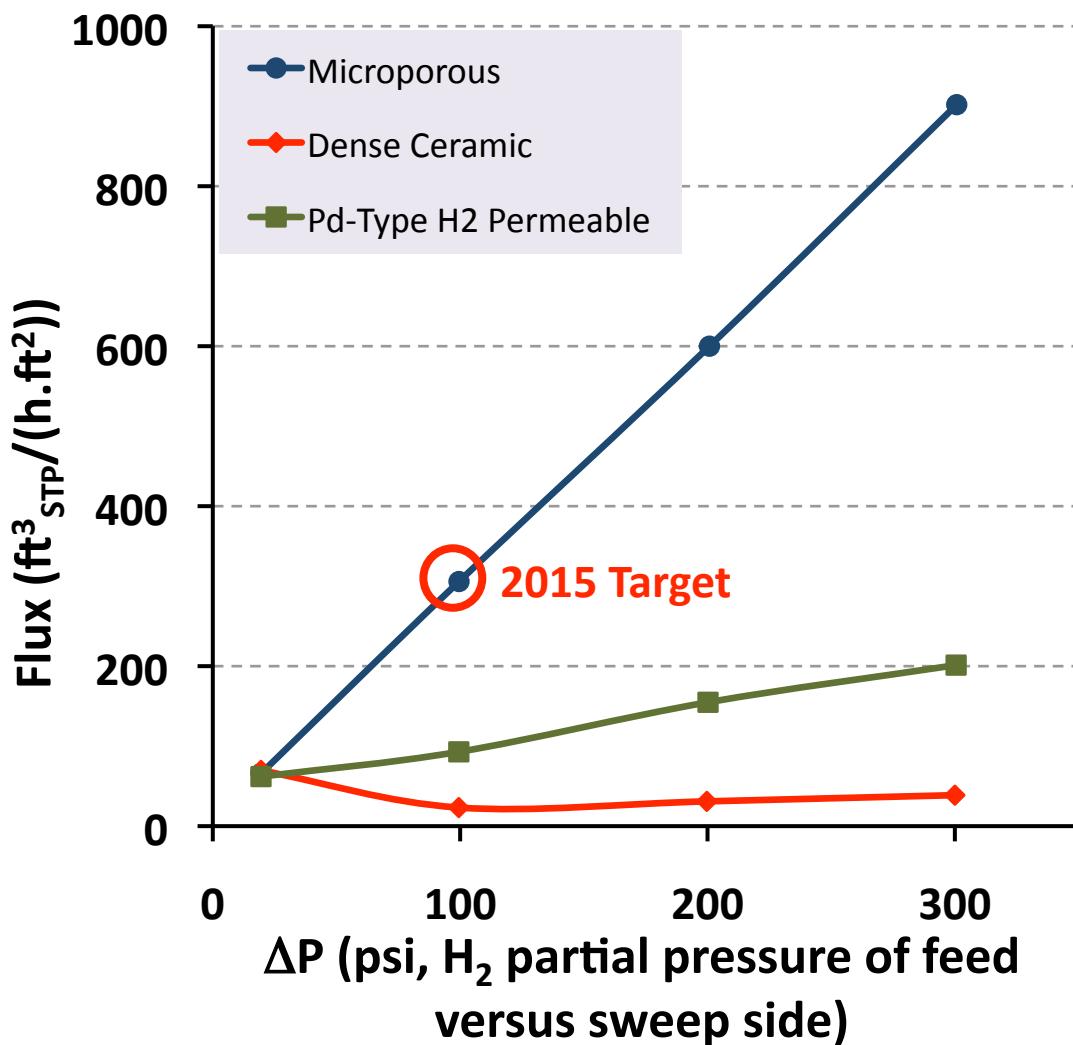
$$\text{Selectivity} = \alpha_{A/B} = \frac{P_A}{P_B} = \left( \frac{S_A}{S_B} \right) \left( \frac{D_A}{D_B} \right)$$

$S_A$  = Solubility coefficient of A

$D_A$  = Diffusion coefficient of A

## 2015 DOE Technical Targets

Microporous membranes show the potential to achieve high H<sub>2</sub> fluxes at low ΔP [1]

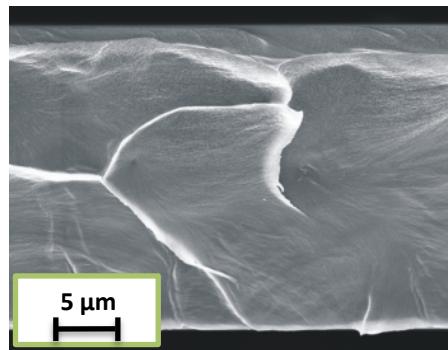


- Hydrogen flux:  $300 \text{ ft}^3_{\text{STP}}/(\text{h.ft}^2)$  @ 100 psi  $\Delta P$  H<sub>2</sub> partial pressure
- Temperature: 250 to 500 °C
- Pressure performance:  $\Delta P$  800 to 1000 psi
- Sulfur tolerance: >100 ppm
- CO tolerance
- Water Gas Shift (WGS) activity
- Hydrogen purity: 99.99%

[1] Hydrogen from coal program: Research, development, and demonstration plan, U. S. DOE, 2009

## Polymeric membranes

- ◆ Lower manufacturing costs
- ◆ High mechanical resistance
- ◆ Lower flux
- ◆ Low selectivity



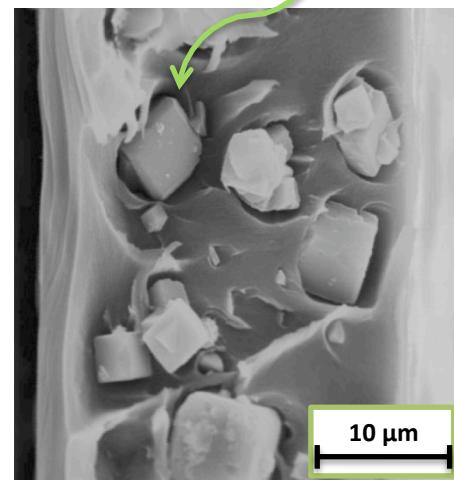
## Inorganic membranes

- ◆ Higher manufacturing costs
- ◆ Low mechanical resistance
- ◆ High flux (5-10 fold higher P)
- ◆ Good selectivity

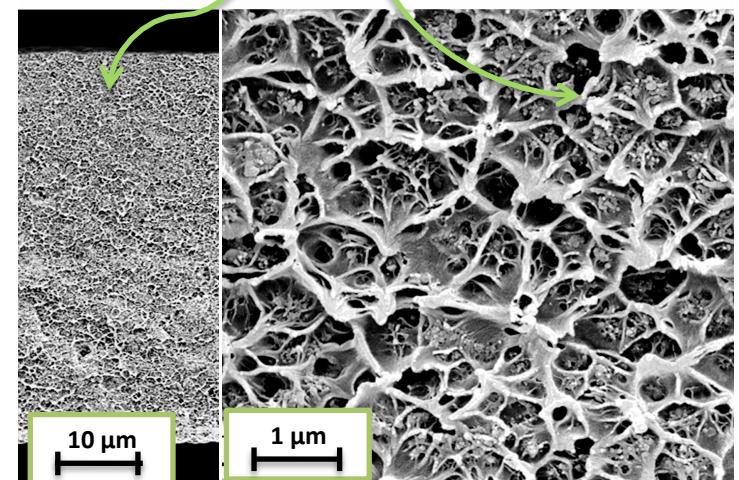
## Mixed-matrix membranes

- ◆ Low manufacturing costs
- ◆ Combines superior separation of inorganic materials with the processability of polymeric materials
- ◆ Possibility to test materials that would not form membranes
- ◆ High loadings may be necessary to overcome polymer permeation properties
- ◆ Challenges with inorganic – organic interface

(sieve-in-a-cage problem)



(Good particle/polymer wetting)





Mixed-Matrix  
Membranes

# UT-Dallas Project

## UTD project objectives (DE-NT0007636)

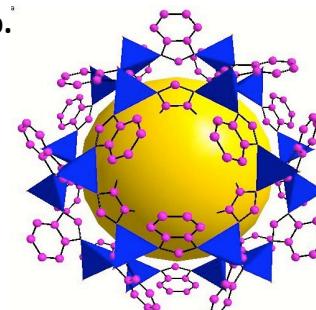
- Prepare novel MMMs based on polymer composites with nanoparticles of zeolitic imidazolate frameworks (ZIFs)
  - Synthesis of ZIFs
  - Synthesis of high performance polymers
  - Fabrication of MMMs
- Evaluate MMMs for separations important to coal gasification (e.g. H<sub>2</sub>, CO, O<sub>2</sub>, CO<sub>2</sub>)
- Test performance of MMMs under operating conditions defined by 2015 DOE targets
  - Construction of high pressure-high temperature permeameter

Targeted ZIFs for H<sub>2</sub> Separations**Inorganic Additive**

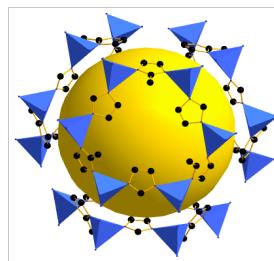
- Stable above 300 °C
- Stable to H<sub>2</sub>O (steam), CO, and H<sub>2</sub>S
- Fabricated as nanoparticles
- Controlled pore size
- Strong interaction with polymer

ZIF	Pore Size (nm)	Pore Aperture (nm)	Sieving
ZIF -7	0.90	0.30	H <sub>2</sub>
ZIF-8	1.10	0.34	H <sub>2</sub>
ZIF-20	1.40	0.45	H <sub>2</sub> , CO <sub>2</sub>
ZIF-69	0.72	0.44	H <sub>2</sub> , CO <sub>2</sub>
ZIF-90 and derivatives	1.12	0.35	H <sub>2</sub>
ZIF-95	24.00	0.36	H <sub>2</sub>
ZIF-100	3.60	0.33	H <sub>2</sub>
MIL-53-It	n/a	0.28	H <sub>2</sub>

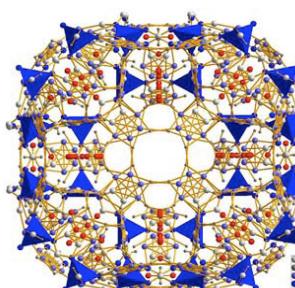
	Kinetic Diameter	Critical Temp.
N <sub>2</sub>	0.36 nm	-147 °C
O <sub>2</sub>	0.34 nm	-118.4 °C
CH <sub>4</sub>	0.38 nm	-82.1 °C
CO <sub>2</sub>	0.33 nm	31 °C
H <sub>2</sub>	0.28 nm	-232.6 °C



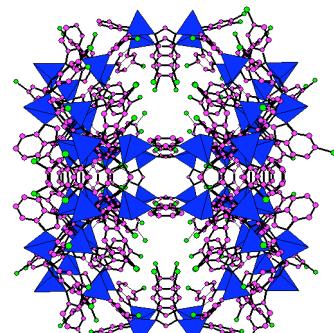
ZIF-7



ZIF-8



ZIF-20

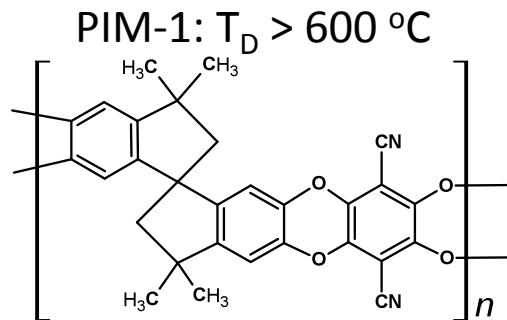


ZIF-95

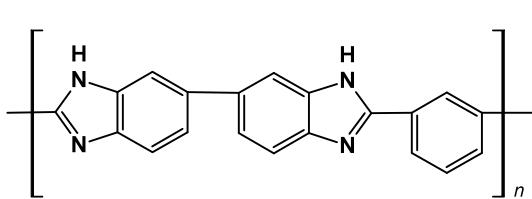
# Targeted Polymers for MMMs

## Polymer

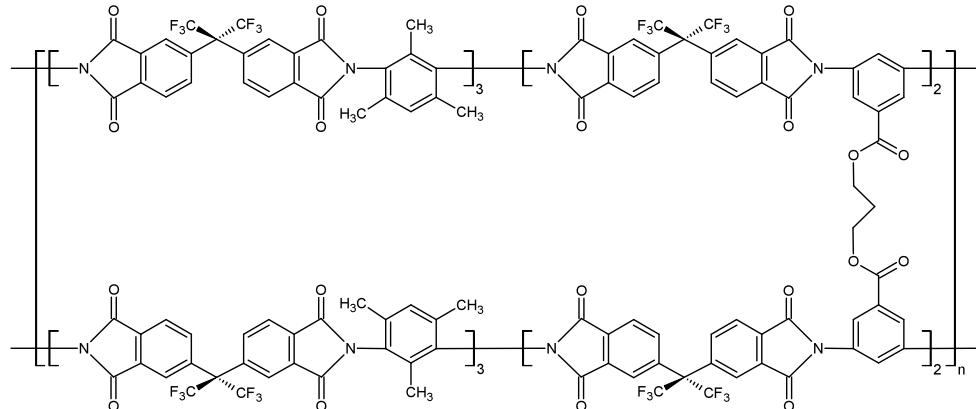
- Stable above 300 °C
- Processable
- Separation properties close to upper bound ( $H_2/CO_2$  separation)
- Stability to  $H_2O$  (steam), CO, and  $H_2S$



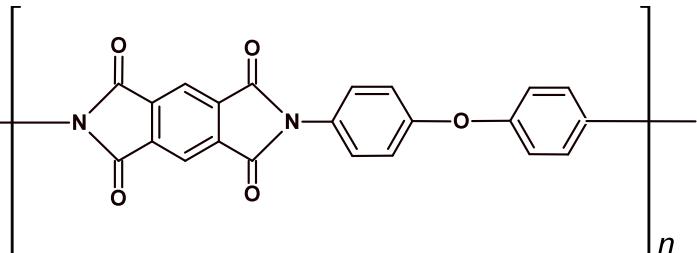
**PBI:  $T_g > 450$  °C**



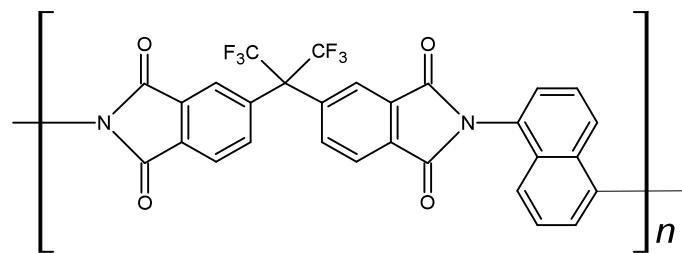
**Cross-linked propane diol monoester (CPDM)  $T_g = 360$  °C**



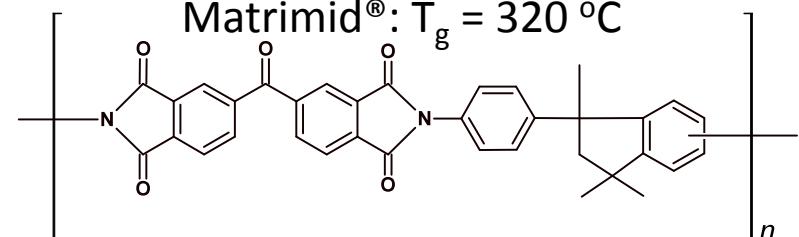
**VTEC (similar to Kapton):  $T_g > 500$  °C**



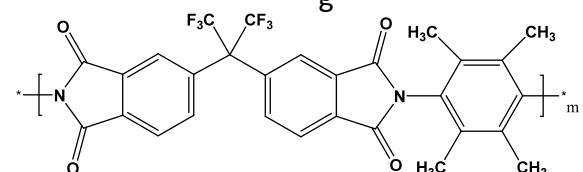
**6FDA-NDA:  $T_g = 430$  °C**



**Matrimid®:  $T_g = 320$  °C**



**6FDA-durene:  $T_g = 425$  °C**



## Diagram showing components of apparatus:

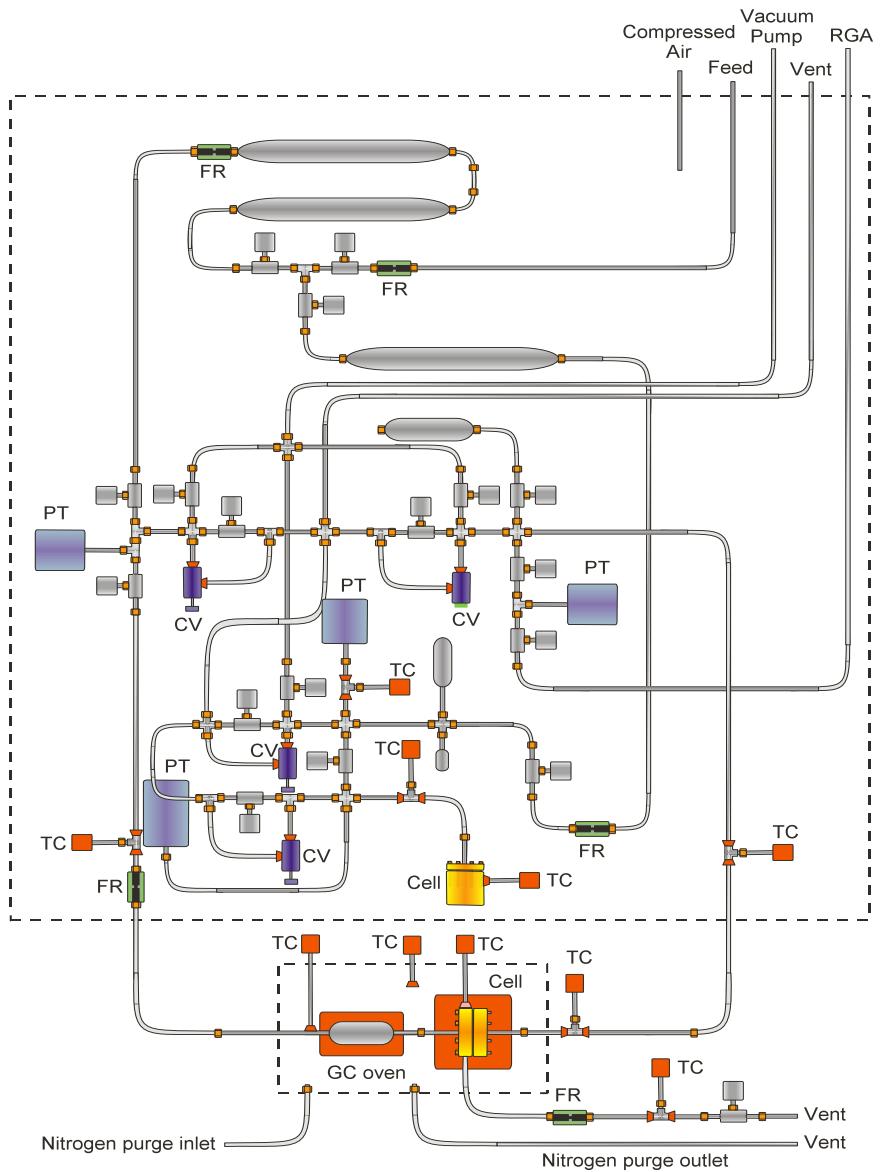
maximum pressure: 65 atm  
temperature: 300 °C  
pressure transducers (PT)  
thermocouples (TC)

## Safety components incorporated into design:

check valves (CV)  
flow restrictors (FR)  
nitrogen purge

## Permeability and solubility cells have their own heaters

Permeation and solubility experiments can be performed simultaneously and independently



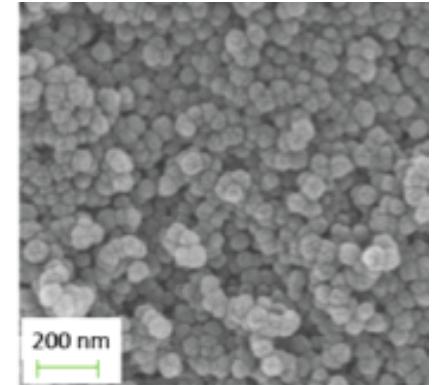
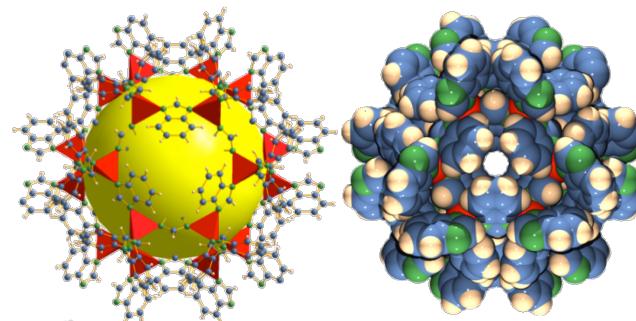
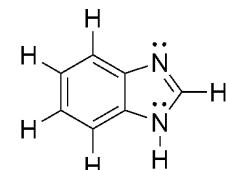
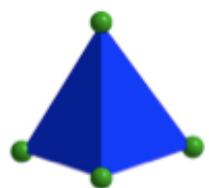


# Previous Results

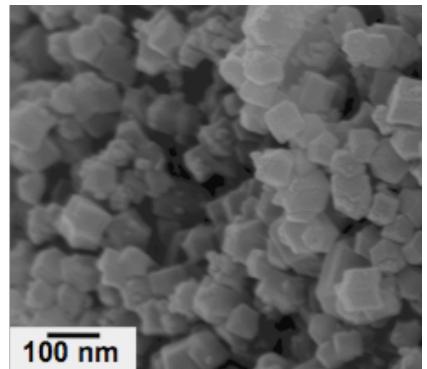
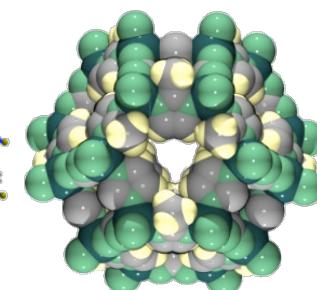
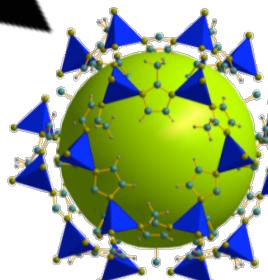
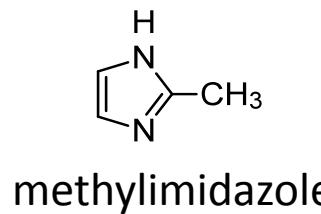
## ZIF-7

- cage size: 9 - 11 Å
  - pore aperture: 3.0 Å
- kinetic diameter  $H_2$  = 2.89 Å  
 $CO_2$  = 3.30 Å

benzimidazole



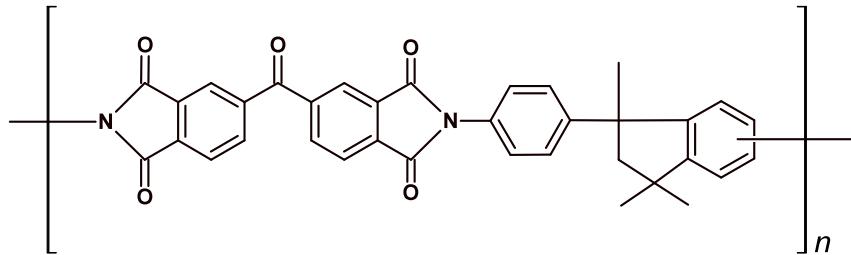
Zn cluster

Stable to steam and  $H_2S$  at 250 °C

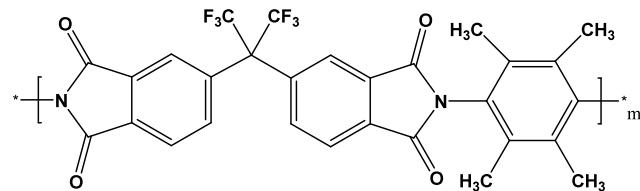
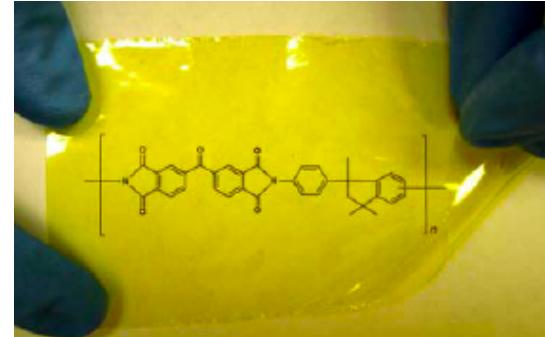
## ZIF-8

- cage size: 11.6 Å
- pore aperture: 3.4 Å
- surface area: >1600 m<sup>2</sup>/g

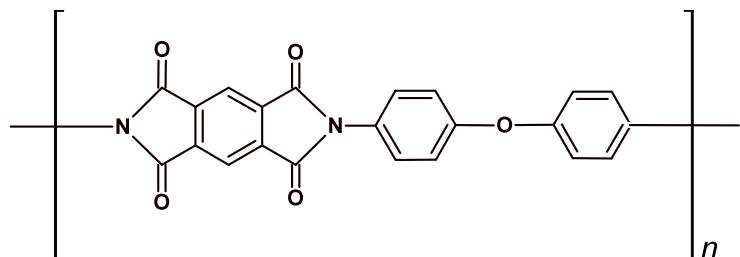
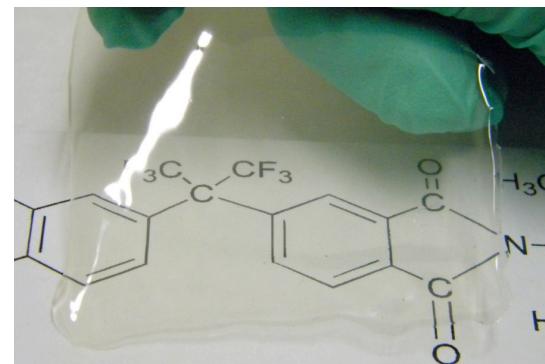
## Polymers for MMMs



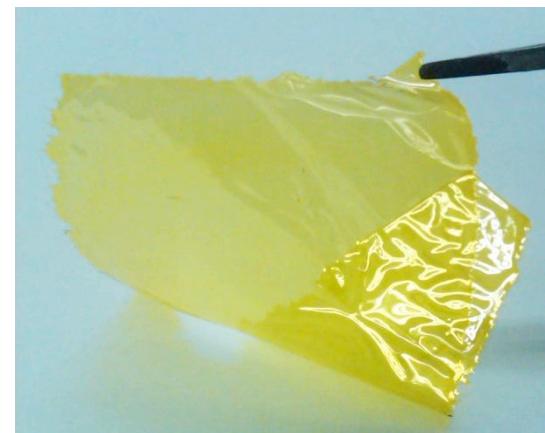
Matrimid®:  $T_g = 320 \text{ }^\circ\text{C}$



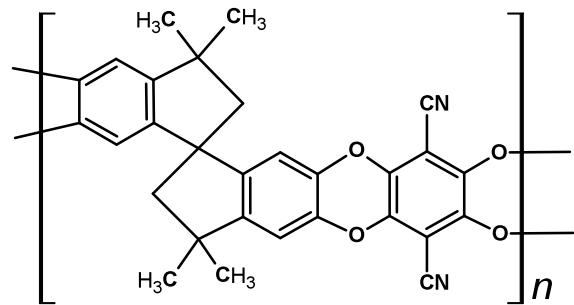
6FDA-durene:  $T_g = 425 \text{ }^\circ\text{C}$



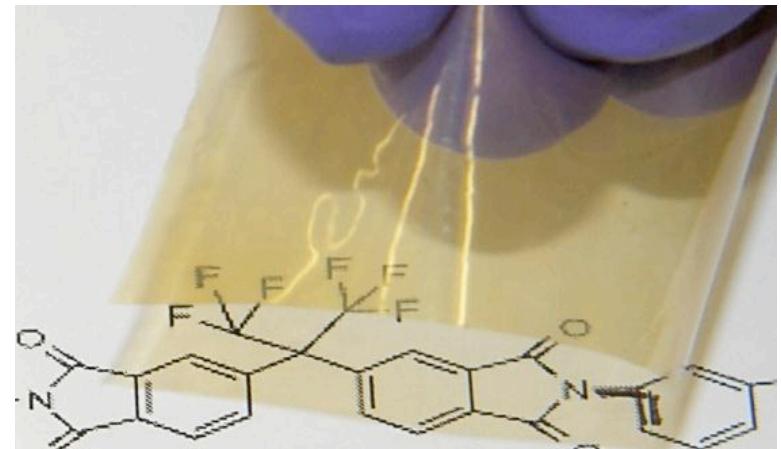
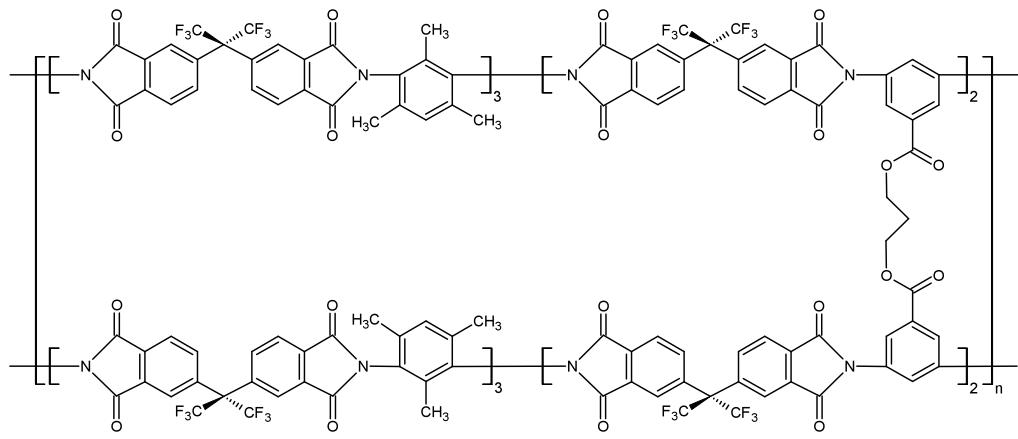
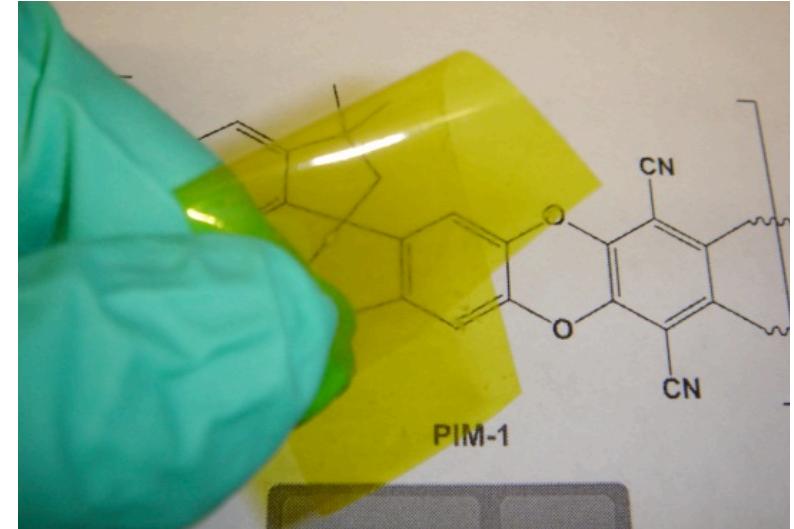
VTEC (similar to Kapton):  $T_g > 500 \text{ }^\circ\text{C}$



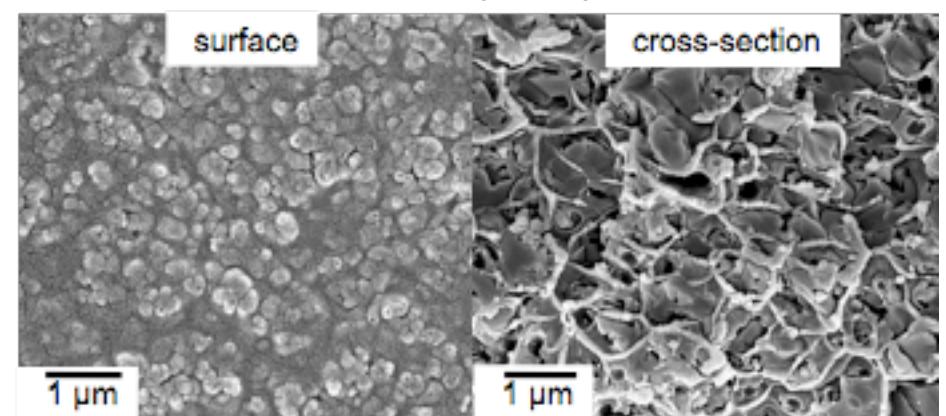
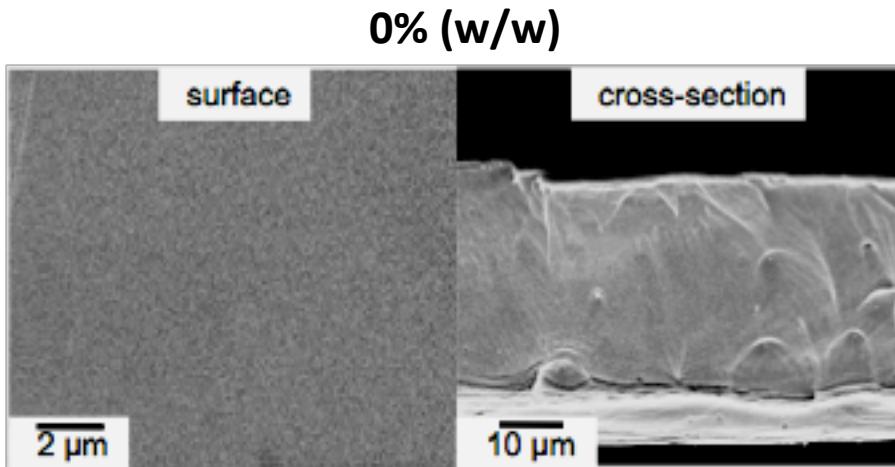
## Polymers for MMMs



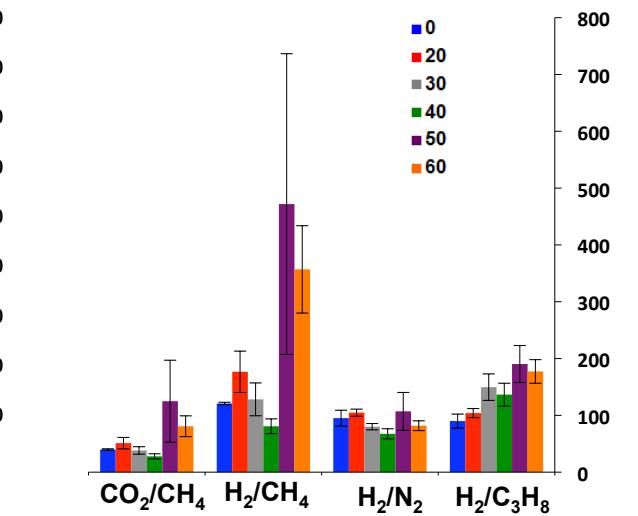
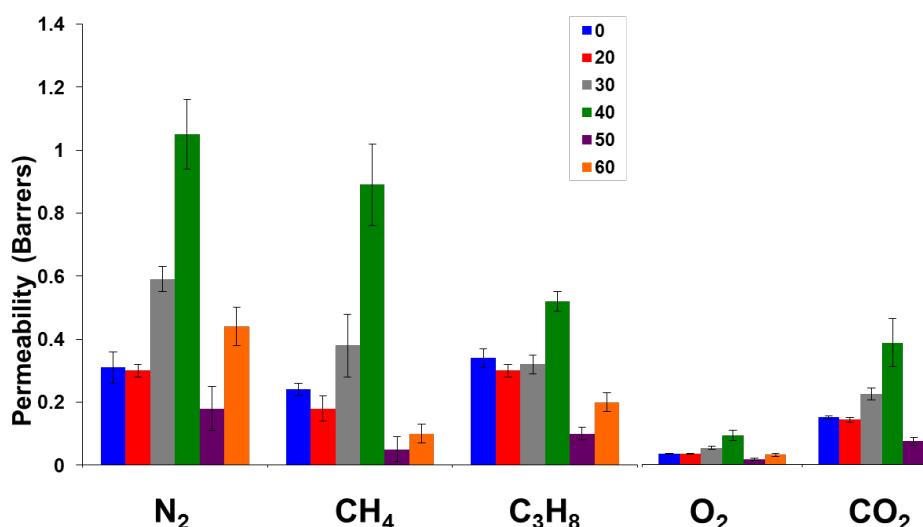
PIM-1:  $T_g > 300 \text{ }^\circ\text{C}$



Cross-linked propane diol monoester (CPDM)  $T_g = 360 \text{ }^\circ\text{C}$



- good dispersion of ZIF-8 material in the polymer matrix
- membrane thickness is 40-50  $\mu\text{m}$



# High Pressure-High Temperature Permeameter



USB data acquisition units provide a fast and easy-to-configure interface

In-line thermocouples provide accurate and fast measurements of gas and cell temperatures

Maximum operating conditions: 65 atm, 400 °C (components operate up to 65 °C)



# New Results

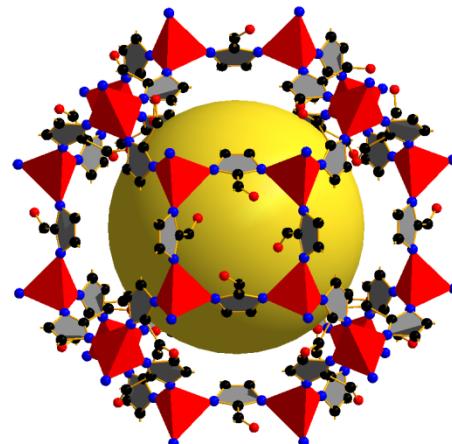
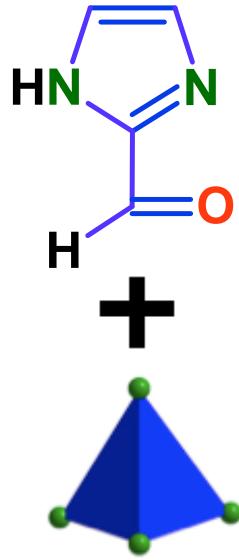


# **Metal-Organic Frameworks and Zeolithic Imidazolate Frameworks**

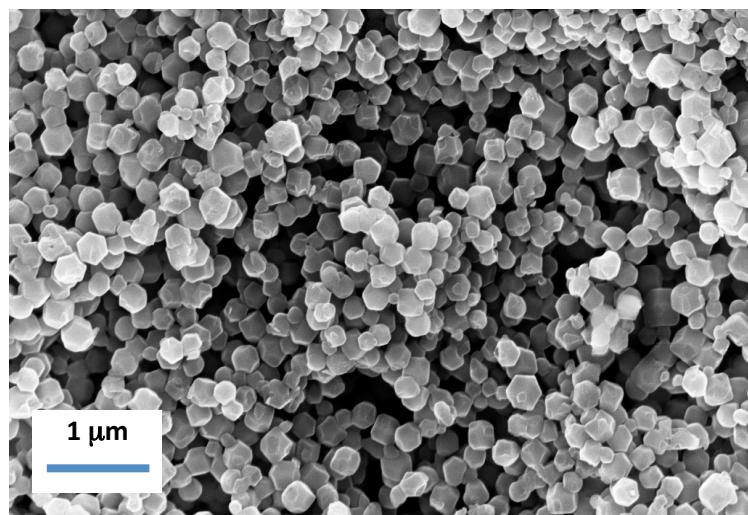
# Mixed-Matrix Membranes

## ZIF-90

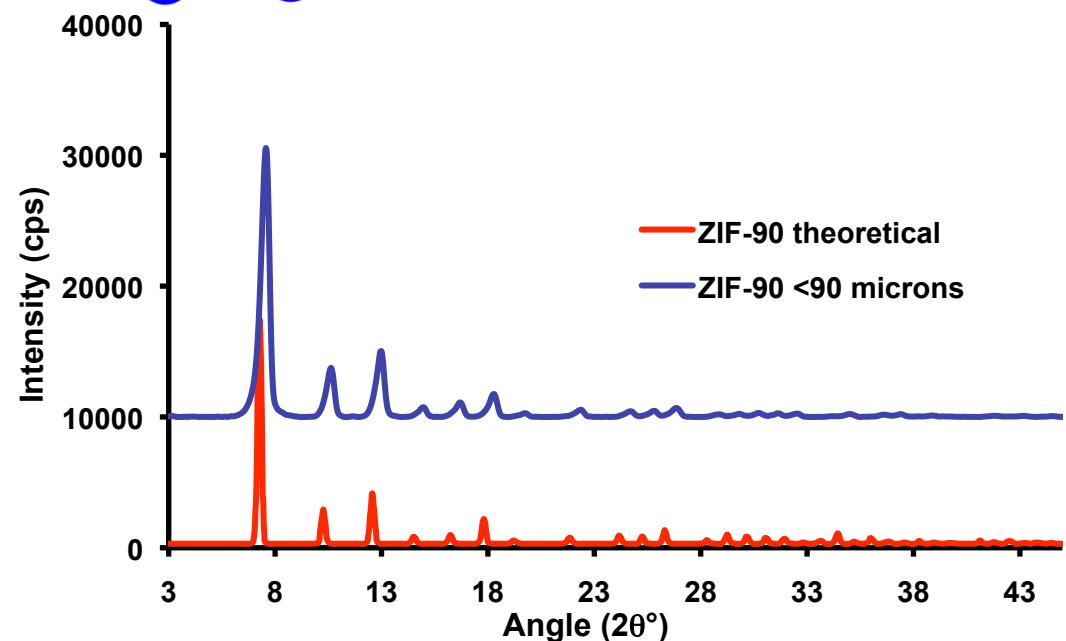
2-Imidazolecarboxaldehyde



Zn cluster



- Pore aperture 0.35 nm
- $H_2/CO_2 = 7$  @ 200 °C
- Stable to 300 °C
- Chemical functionalization of carboxaldehyde for improved ZIF/polymer interface



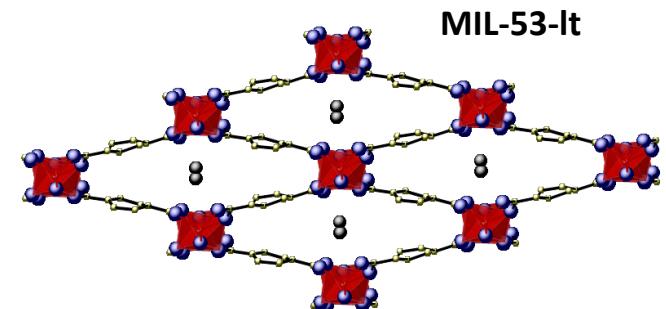
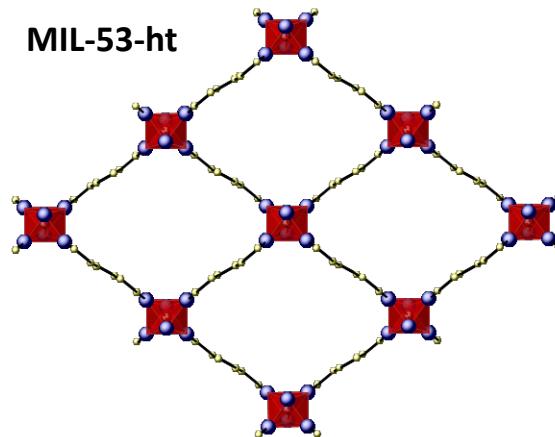
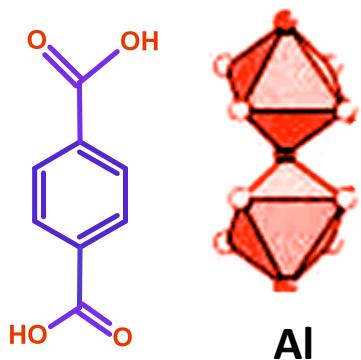
Mixed-Matrix

# Membranes

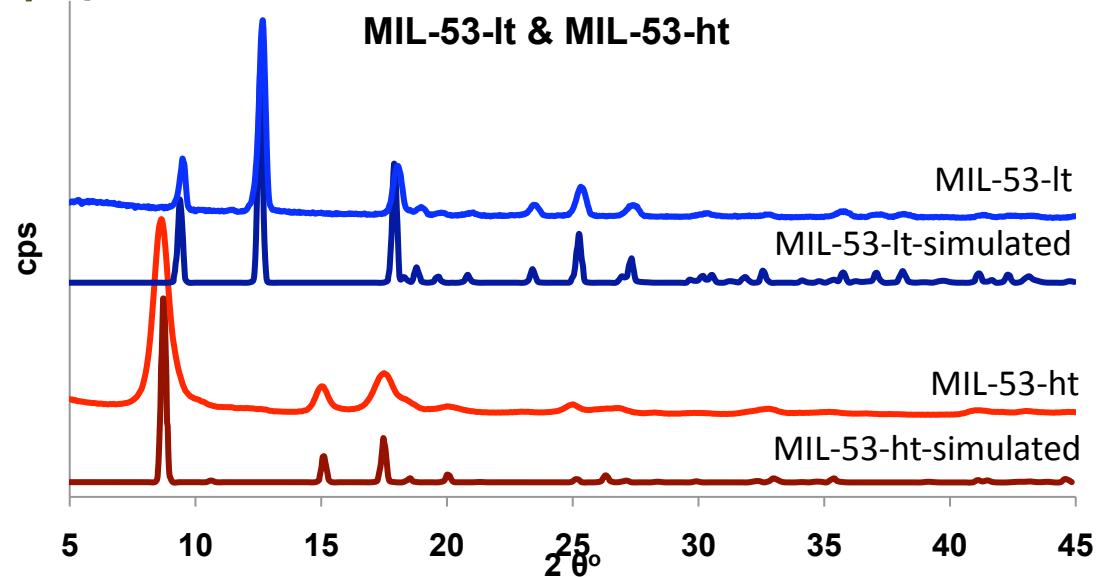
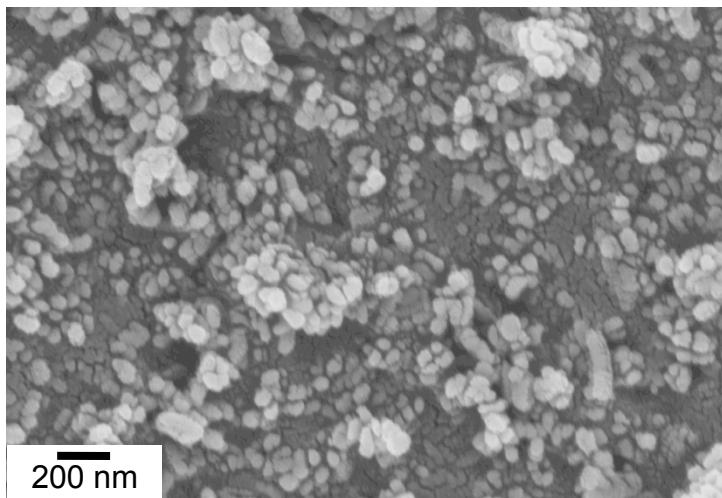
MIL-53

MIL-53 synthesized in:  
high temperature (ht) form with 0.85 nm pore size  
low temperature (lt) form with 0.26 pore size

Material is stable to 500 °C



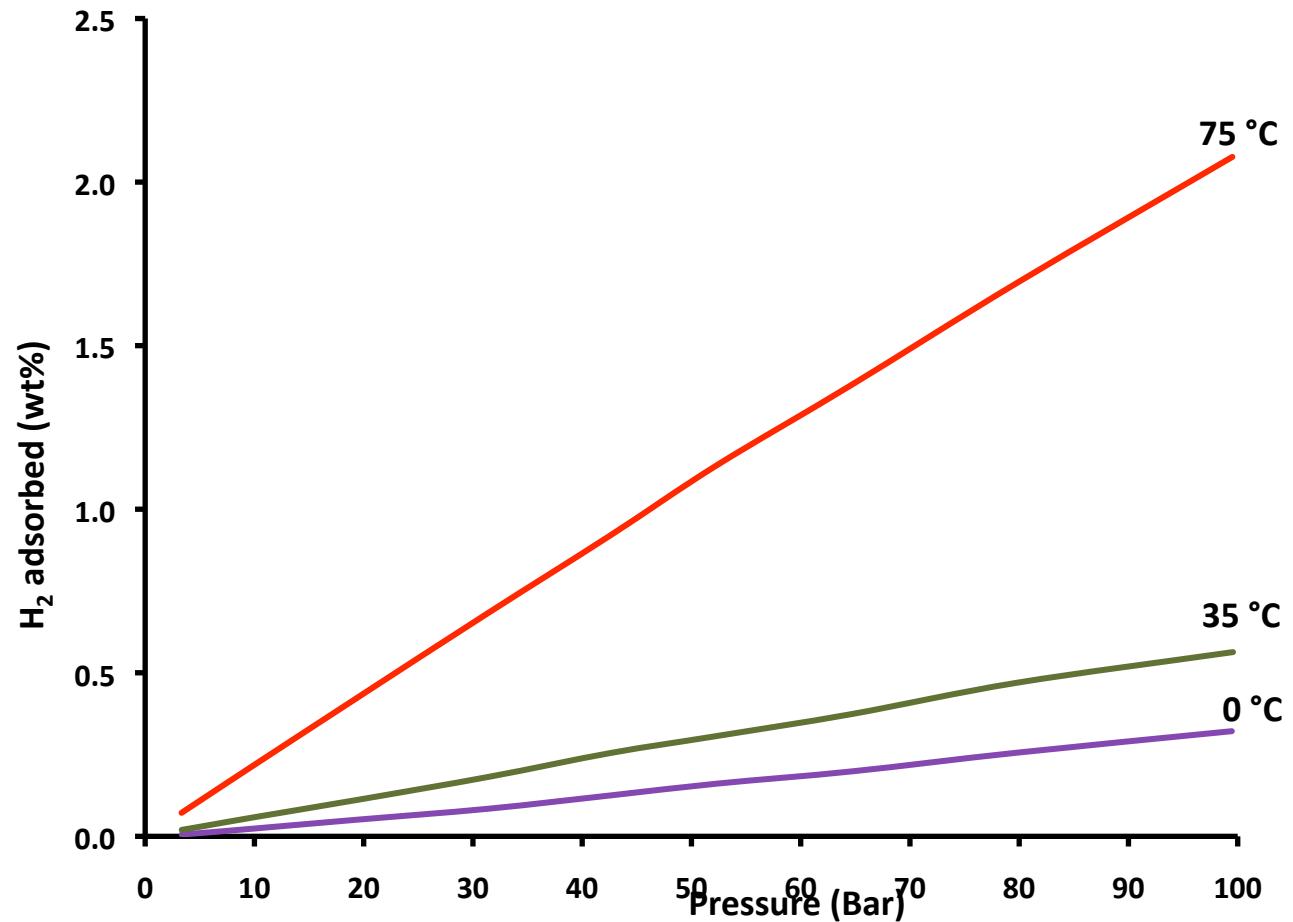
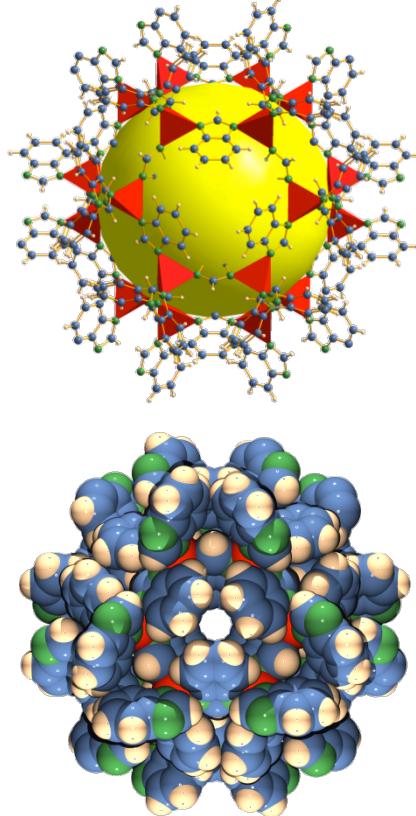
SEM image



# Mixed-Matrix Membranes

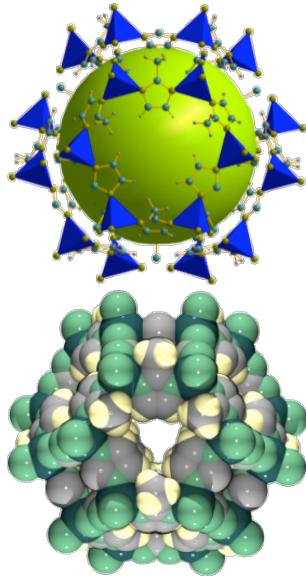
## H<sub>2</sub> Sorption in ZIF-7

H<sub>2</sub> sorption in ZIF-7 increased at higher temperatures, contrary to common trends observed for other porous materials. The increased gas sorption could be due to the expansion of the pore aperture induced by the rotation of the linker.

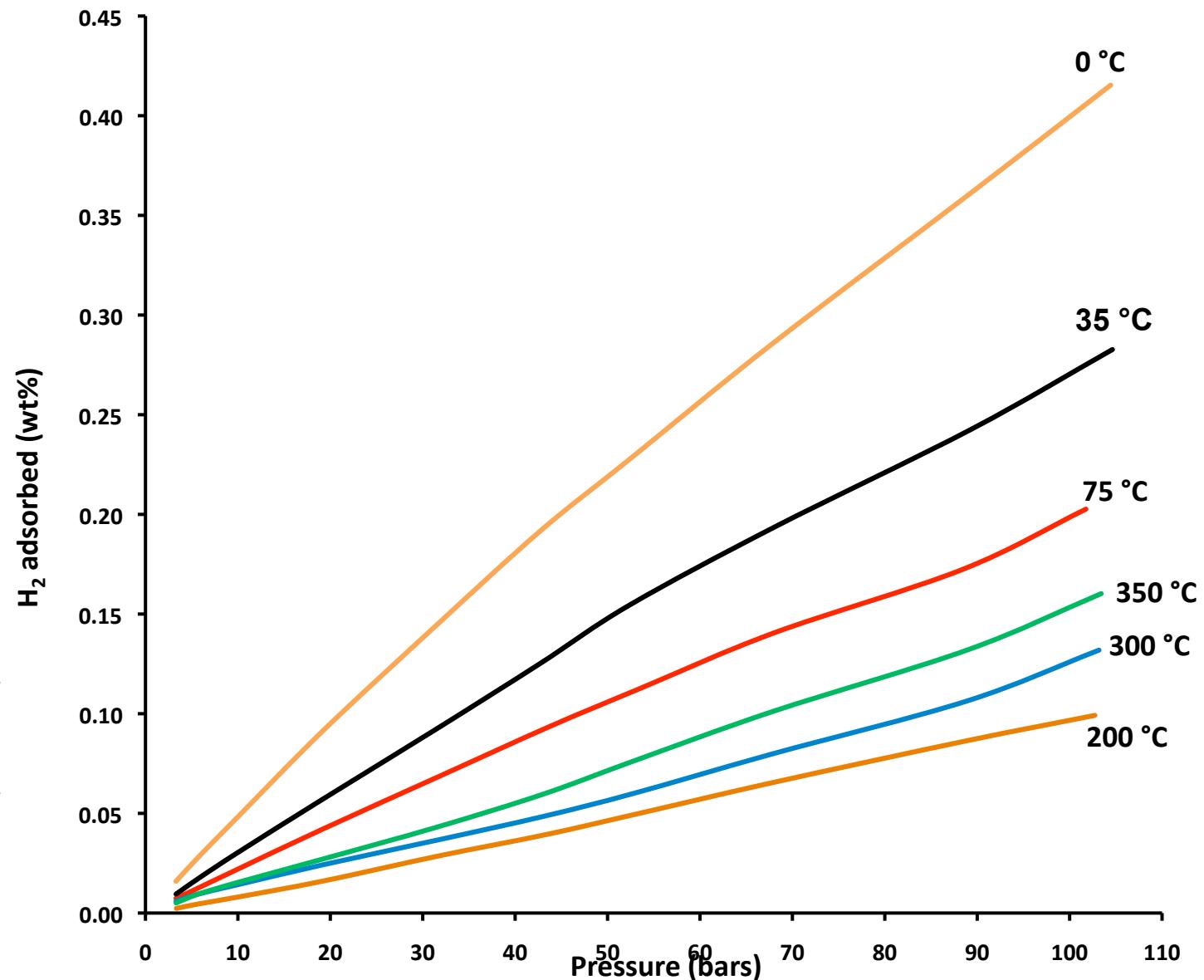


# Mixed-Matrix Membranes

## H<sub>2</sub> Sorption in ZIF-8

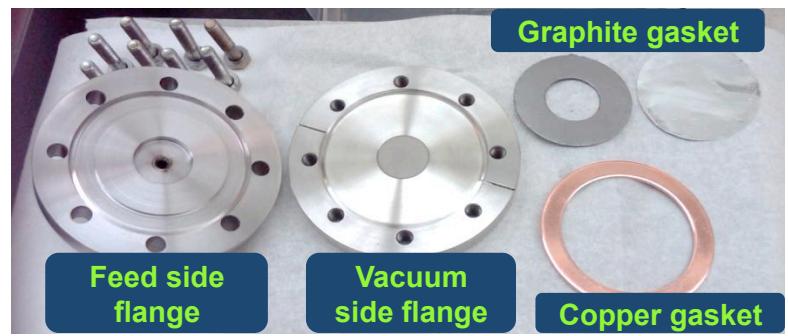
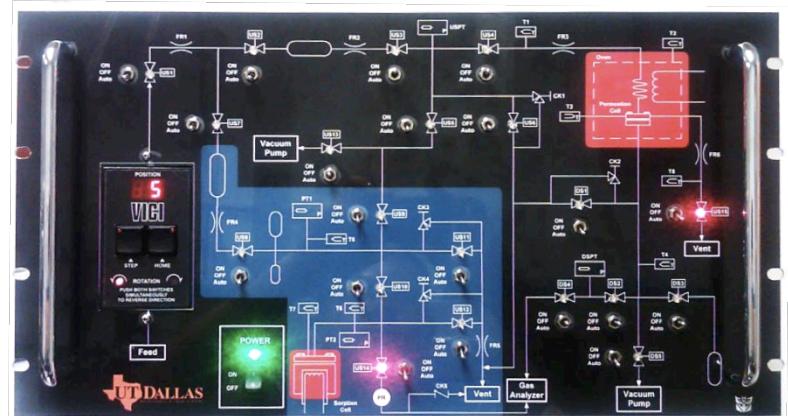


The sorption isotherms of H<sub>2</sub> in ZIF-8 from 0 to 200 °C show a continuous decrease in the amount of H<sub>2</sub> adsorbed, but at temperatures above 200 °C, the amount of H<sub>2</sub> adsorbed increases.





# **High Temperature-High Pressure Permeation Experiments**

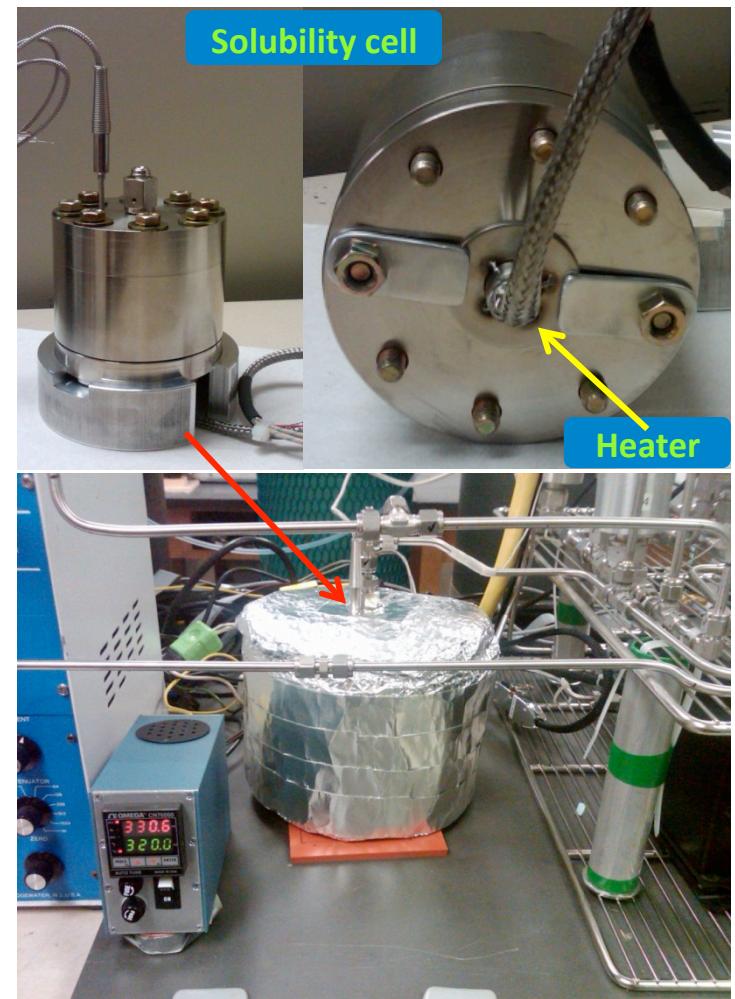
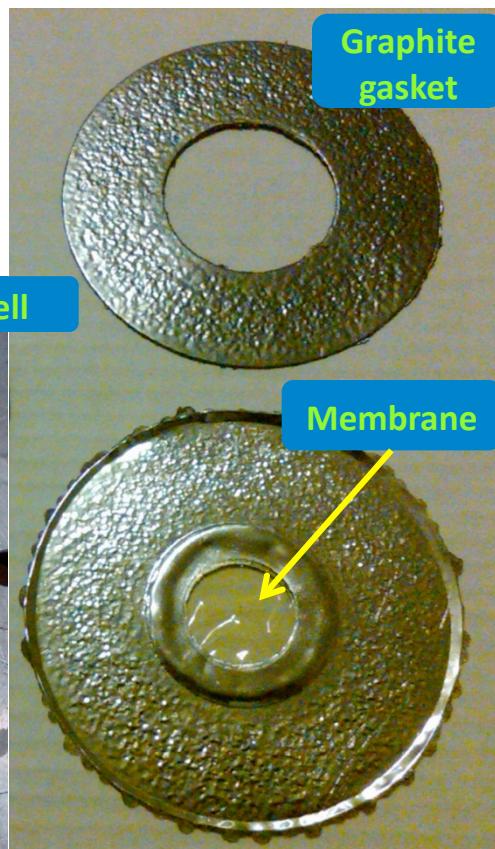
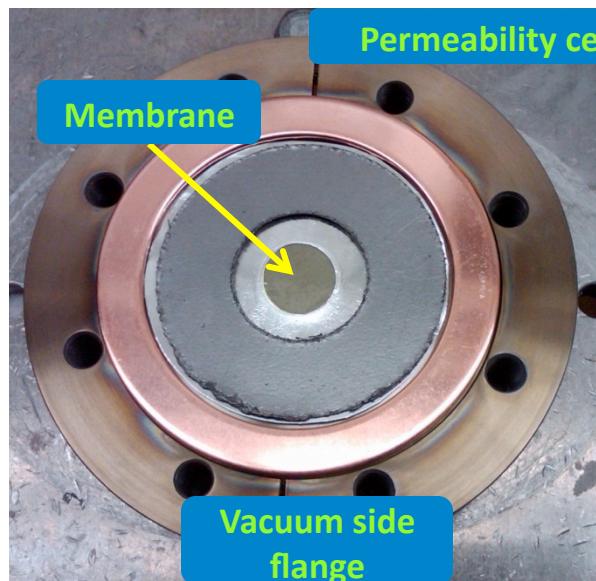
High Pressure-High Temperature  
Permeameter

# Mixed-Matrix Membranes

## HPHT Cells

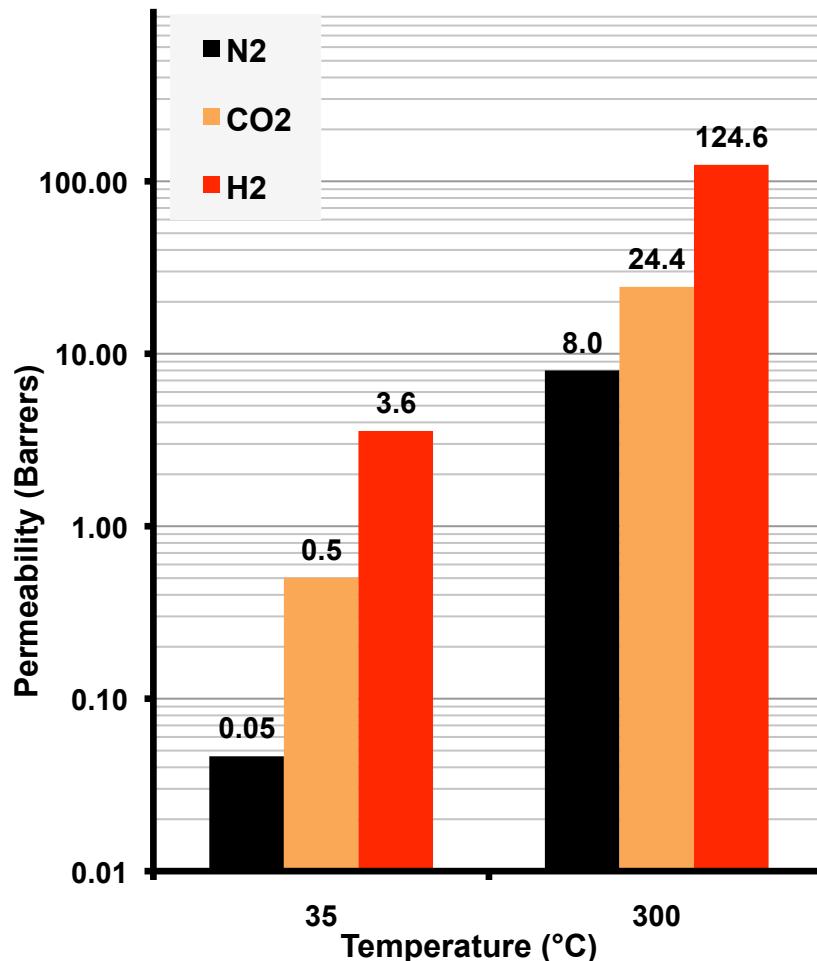
For permeability experiments, the membrane was mounted with aluminum tape and sealed with a graphite gasket that was compressed with the flanges.

The solubility cell incorporated a cartridge heater close to the sample to improve heat transfer.

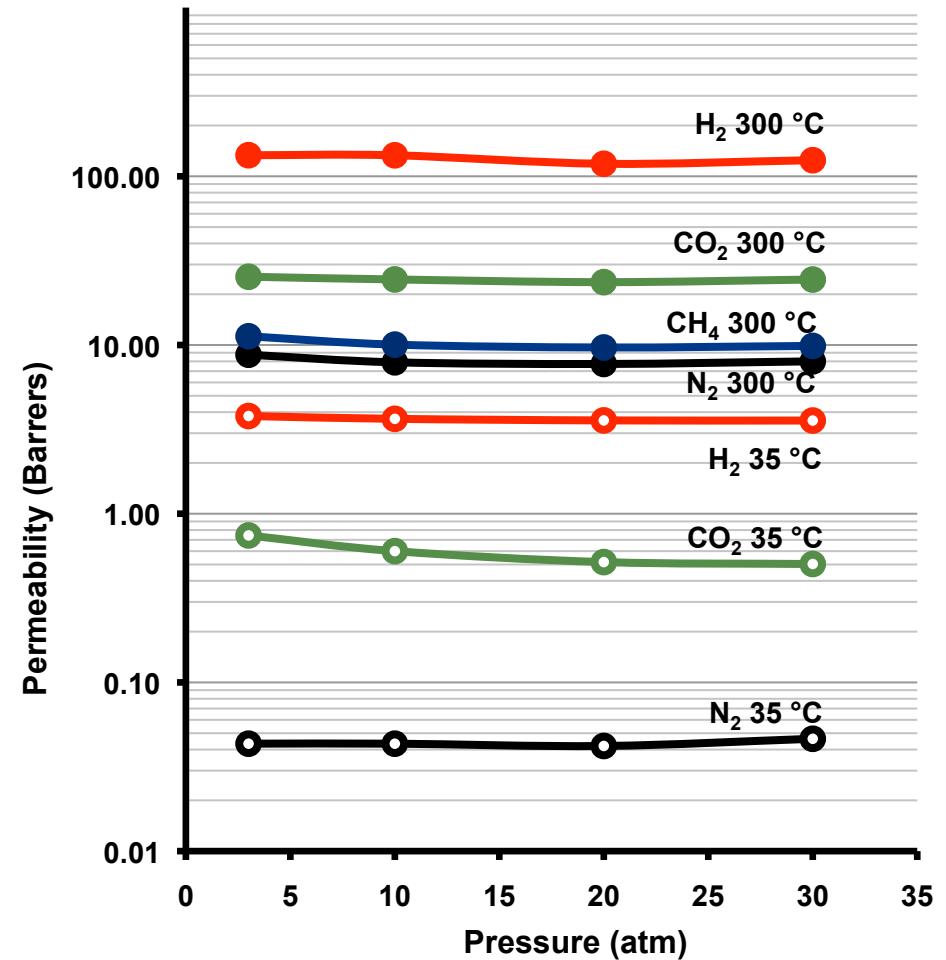


Permeability in VTEC at 35 °C and 300 °C  
and from 3 to 30 atm

VTEC PI-1388 membranes exhibited increased gas permeability with increasing temperature from 35 to 300 °C.  
Permeability was independent of pressure at a given temperature.



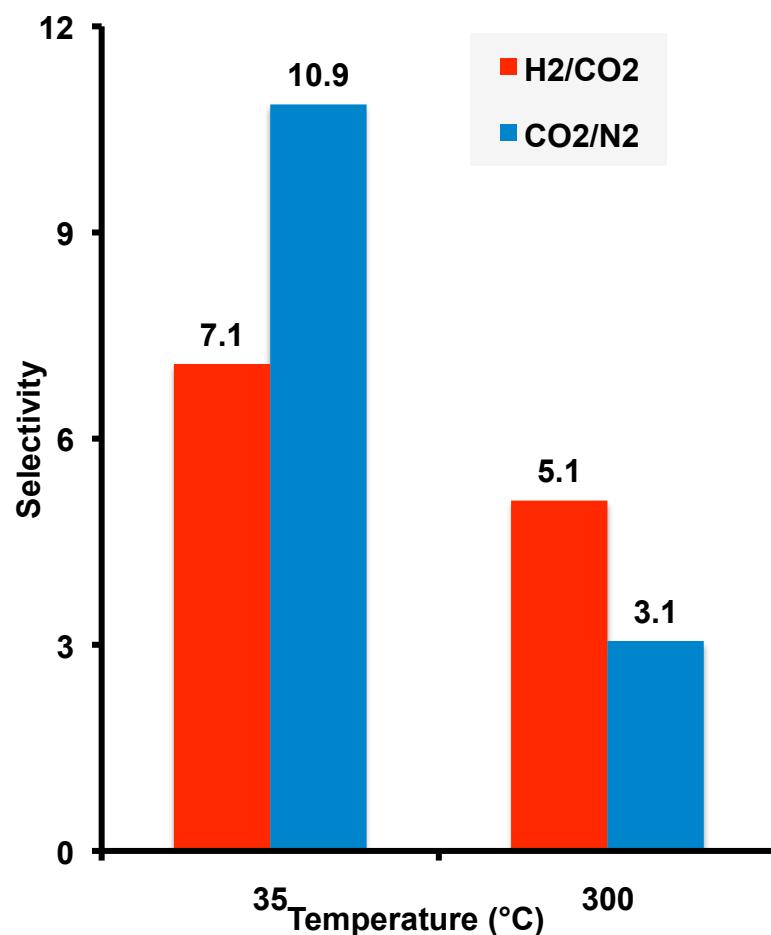
Permeability of VTEC membranes at 30 atm at 35 °C and 300 °C.



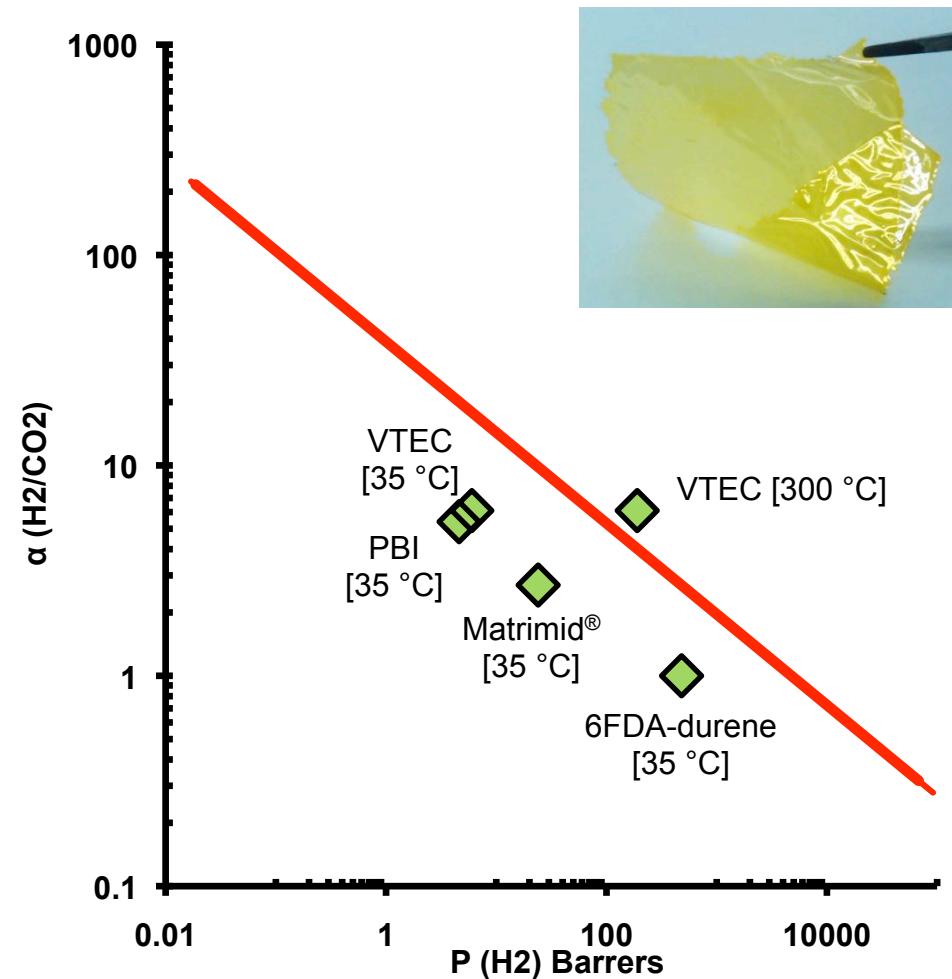
Permeability vs. pressure for VTEC membranes from 3 to 30 atm at 35 °C and 300 °C.

Permeability in VTEC at 35 °C and 300 °C  
and from 3 to 30 atm

Decreases in both H<sub>2</sub>/CO<sub>2</sub> and CO<sub>2</sub>/N<sub>2</sub> selectivities at higher temperatures.  
The H<sub>2</sub>/CO<sub>2</sub> selectivity at 300 °C placed VTEC above the Robeson upper bound.



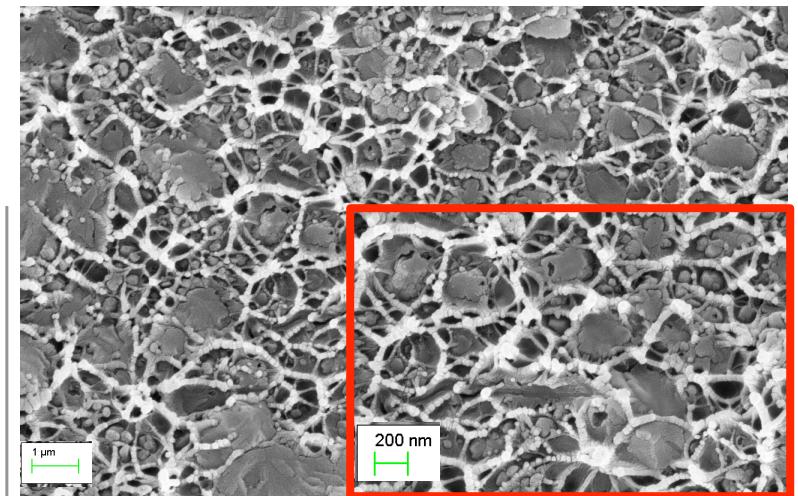
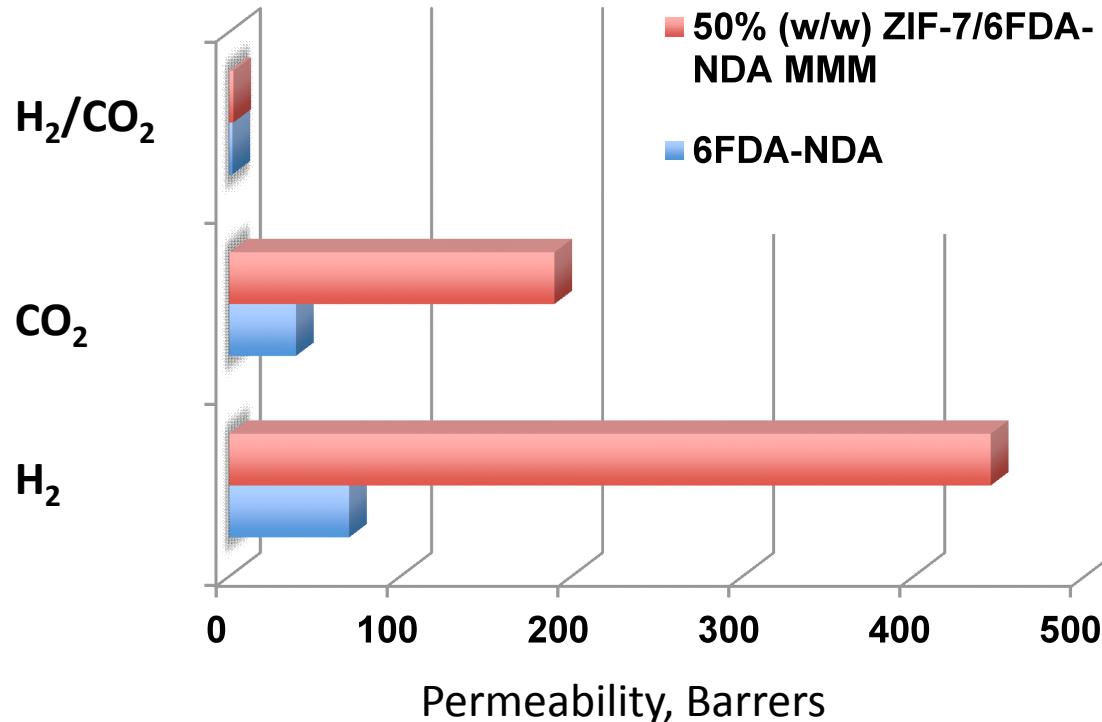
H<sub>2</sub>/CO<sub>2</sub> and CO<sub>2</sub>/N<sub>2</sub> selectivities at 30 atm.



Robeson plot for H<sub>2</sub>/CO<sub>2</sub> separations.



# **Mixed-Matrix Membranes**

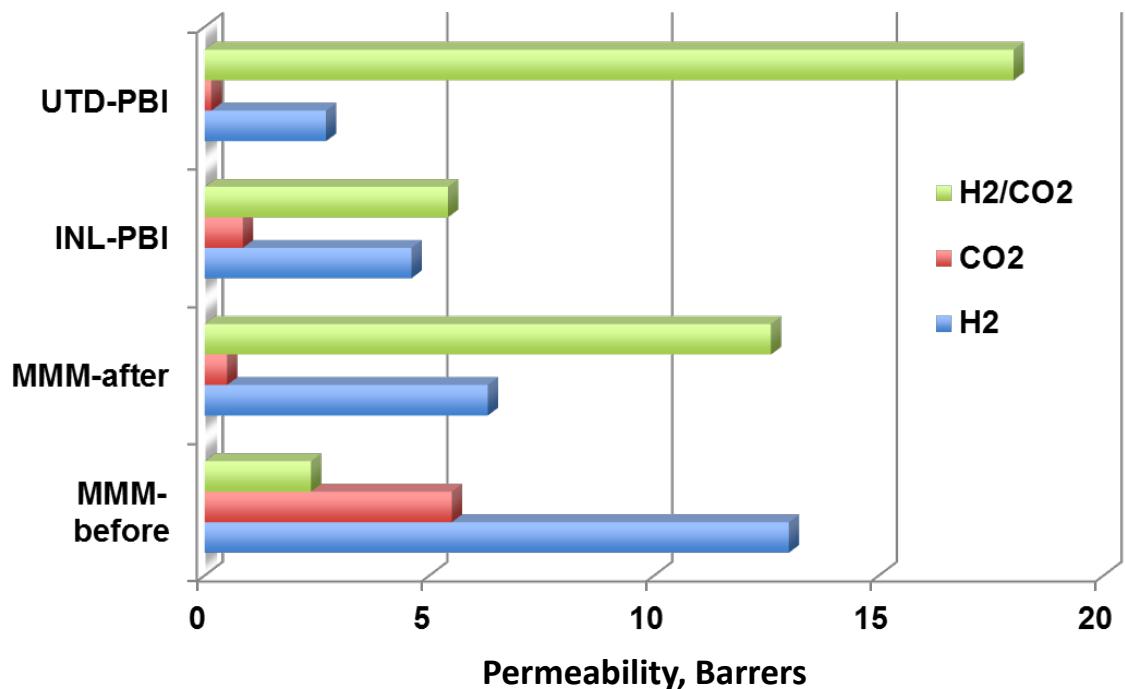
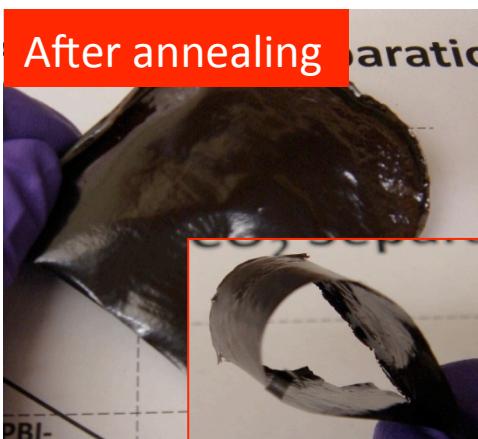


SEM image of a 50% (w/w)  
ZIF-7/6FDA-NDA MMM

Permeabilities and  $\alpha \text{H}_2/\text{CO}_2$  at 35 °C and 3 atm

- Incorporation of ZIF-7 into the highly permeable 6FDA-NDA further increased its permeability
- $\text{H}_2/\text{CO}_2$  selectivity was maintained at ~2

## ZIF-8/PBI MMM



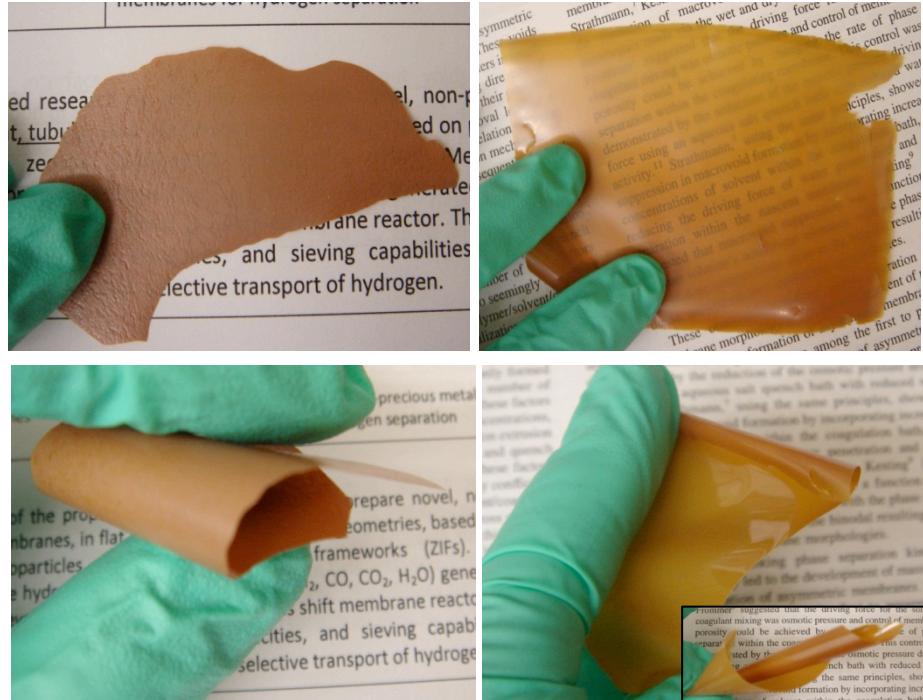
- Annealing 35% (w/w) ZIF-8/PBI MMM at 250 °C changed color from brown to black

- Addition of 35% (w/w) ZIF-8 increased H<sub>2</sub> permeability and decreased H<sub>2</sub>/CO<sub>2</sub> selectivity
- Annealing at 250 °C increased H<sub>2</sub>/CO<sub>2</sub> selectivity, and decreased H<sub>2</sub> permeability

INL-PBI: Klaehn, et al. CO<sub>2</sub> separation using thermally optimized membranes: A comprehensive project report (2000 – 2007). INL-CRADA Report.

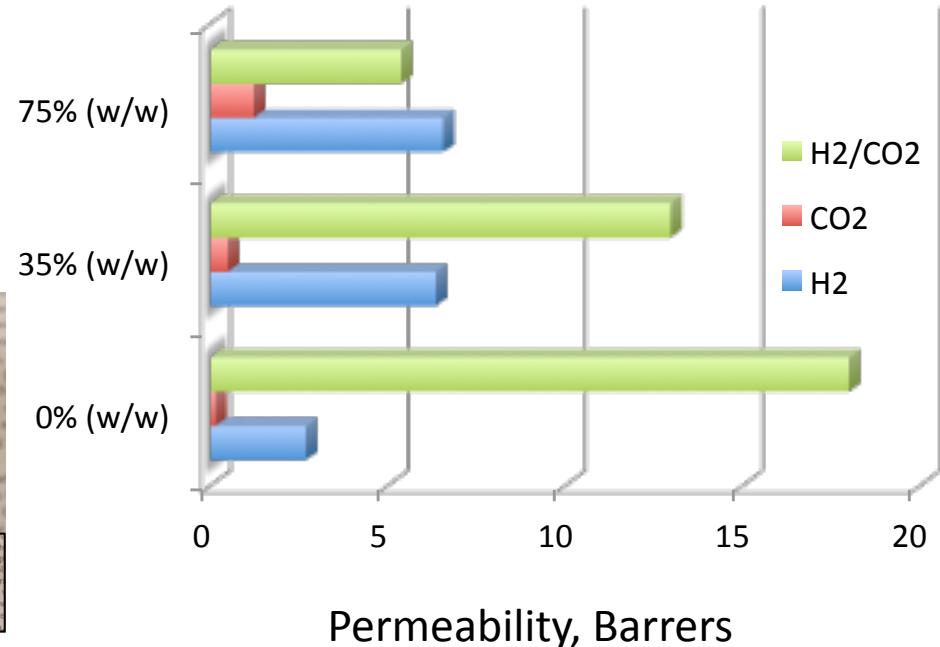
UTD-PBI: Annealed at 250 °C, tested at 35 °C and 3 atm

## ZIF-8/PBI MMM



75% (w/w)

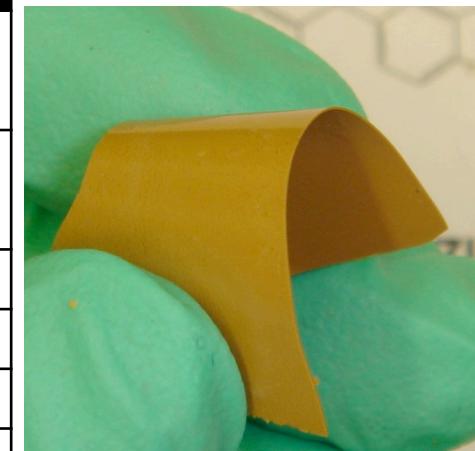
35% (w/w)



- Increasing the ZIF loading from 0 to 35 % (w/w) increases H<sub>2</sub> permeability
- A further increase to 75% (w/w) loading maintains the H<sub>2</sub> permeability but is accompanied by decrease in H<sub>2</sub>/CO<sub>2</sub> selectivity

## ZIF-8/PBI-Matrimid® Blend MMM

Membrane	H <sub>2</sub>	CO <sub>2</sub>	H <sub>2</sub> /CO <sub>2</sub>
<b>50% (w/w) ZIF-8/75:25 wt% PBI-Matrimid®</b>	6.3	1.9	3.30
<b>50% (w/w) ZIF-8/50:50 wt% PBI-Matrimid®</b>	12.5	4.8	2.60
<b>50:50% wt PBI-Matrimid®</b>	13.0	3.1	4.19
<b>75:25% wt PBI-Matrimid®</b>	5.06	0.75	6.70
<b>PBI<sup>1</sup></b>	4.6	0.85	5.40
<b>Matrimid<sup>®2</sup></b>	24.0	9.0	2.70
<b>50% (w/w) ZIF-8/Matrimid<sup>®3</sup></b>	17.0	5.0	3.40
<b>Knudsen</b>	-	-	4.70



**50% (w/w) ZIF-8 in  
50:50% wt PBI-Matrimid® blend**

1. INL-CRADA Final Report 2008.
2. Perez, et al. Mixed-matrix membranes containing MOF-5 for gas separations. *J. Membr. Sci.* **2009**, 328, 165-173.
3. Ordonez, et al. Molecular sieving realized with ZIF-8/Matrimid® mixed-matrix membranes, *J. Membr. Sci.* **2010**, 28-37.

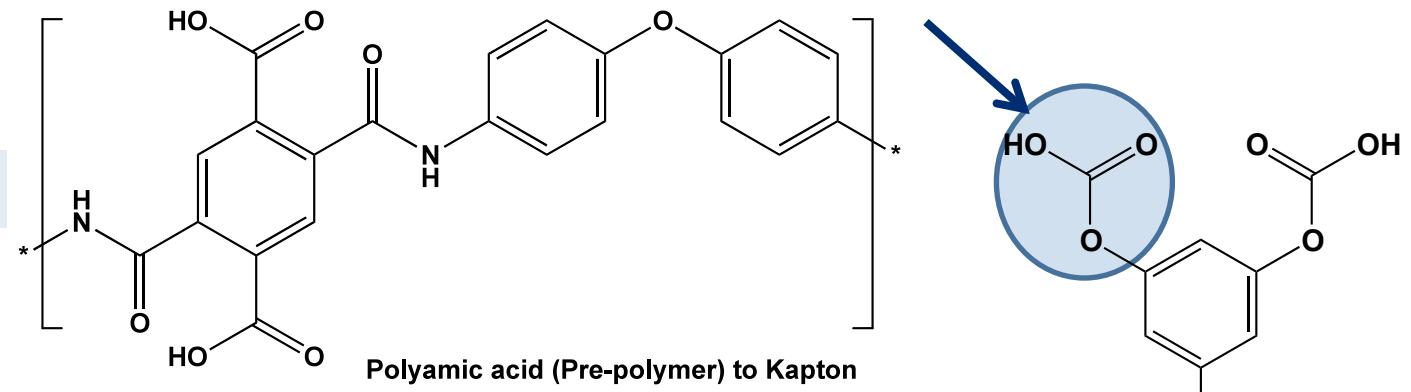
- PBI-Matrimid® blends prepared with PBI containing 1.5 wt% LiCl – P's differ from reported
- Incorporation of ZIF-8 into the blend decreased both P and  $\alpha$ : formation of defects
- Defects can be minimized by annealing at higher T

## ZIF-8/VTEC PI-1388 MMM

## Gelation in MMM



No gelation  
50% (w/w) ZIF-8/  
VTEC PI-1388 MMM

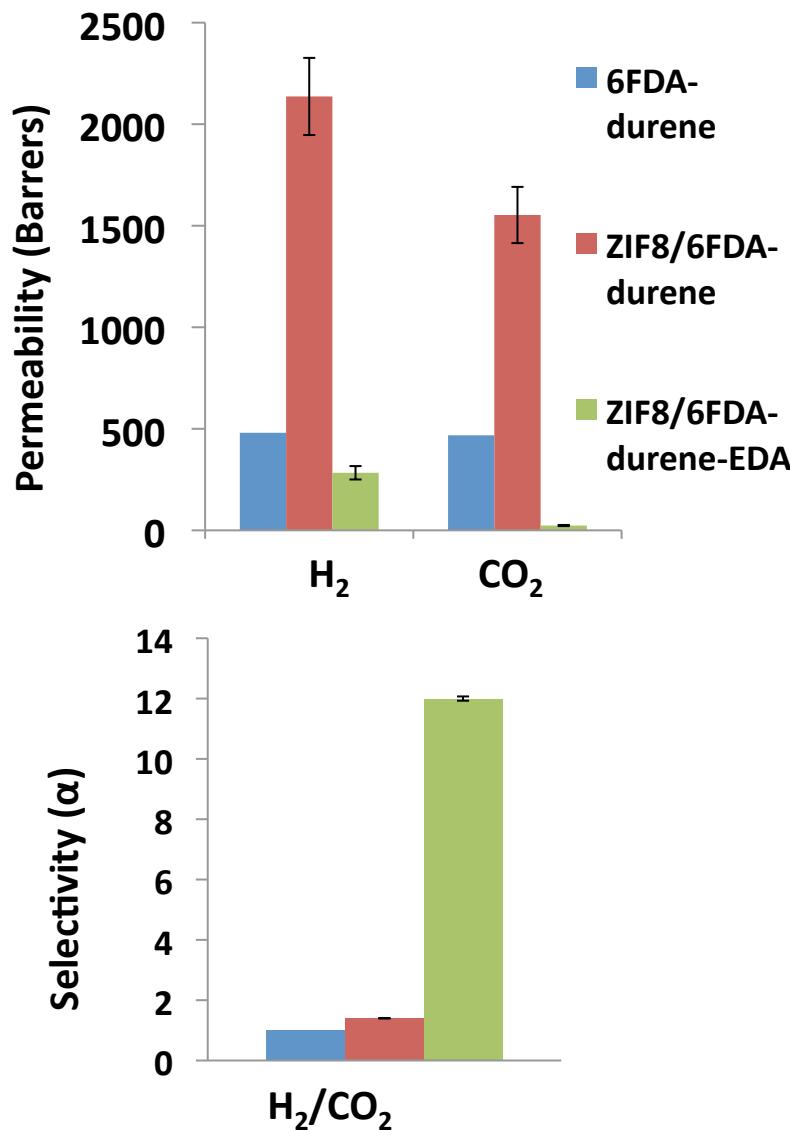


- Carboxylate group in VTEC attacks  $Zn^{2+}$  in ZIF-8
- Incorporation of 12-BDC provides the  $-COOH$  group to avoid gelation

## Gas Permeability and Selectivity Properties

Gas	Permeability		$H_2/CO_2$ Selectivity	
	Treated ZIF-8/ VTEC MMM	Pure VTEC PI-1388	Treated ZIF-8/VTEC MMM	Pure VTEC PI-1388
$H_2$	1703	3.97		
$CO_2$	550	0.53	3.10	7.49

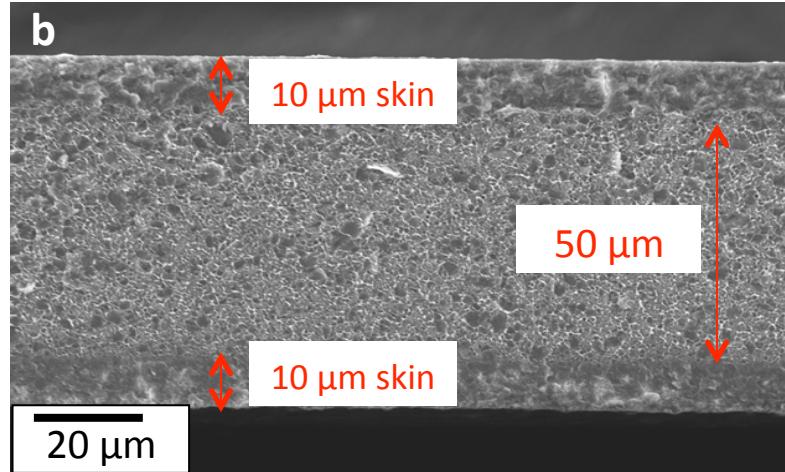
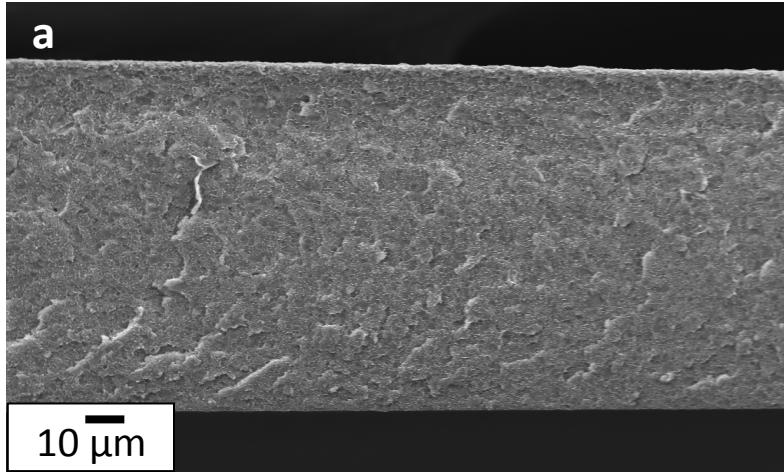
## ZIF-8/6FDA-Durene MMM



Membrane	H <sub>2</sub> (Barrers)	H <sub>2</sub> /CO <sub>2</sub>
6FDA-durene	480.4	1.0
6FDA-durene - EDA	52.1	144
ZIF-8/6FDA- durene	2137 ± 190	1.4 ± 0.0
ZIF-8/6FDA-durene-EDA	283.4 ± 33.0	12.0 ± 0.1
Asymmetric ZIF-8/6FDA-durene spin coated EDA (3 min)	505	18
6FDA-durene <sup>1</sup>	585.4	0.8
6FDA-durene - EDA <sup>2</sup>	32.6	102
ZIF-8 <sup>3</sup>	1726	4.5
Knudsen value		4.7

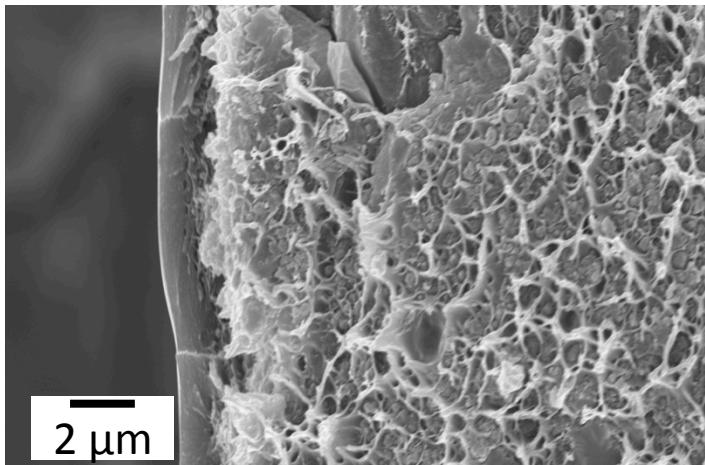
- Kanehashi, S.; Nakagawa, T.; Nagai, K.; Duthie, X.; Kentish, S.; Stevens, G. *Journal of Membrane Science* **2007**, *298*, 147-155
- Shao, L.; Lau, C.-H.; Chung, T.-S *International Journal of Hydrogen Energy* **2009**, *34*, (20), 8716-8722
- Bux, H.; Liang, F.; Li, Y.; Cravillon, J.; Wiebcke, M.; Caro, J. *J.Am.Chem.Soc.* **2009**, *131*, 16000-16001

## Symmetric crosslinking



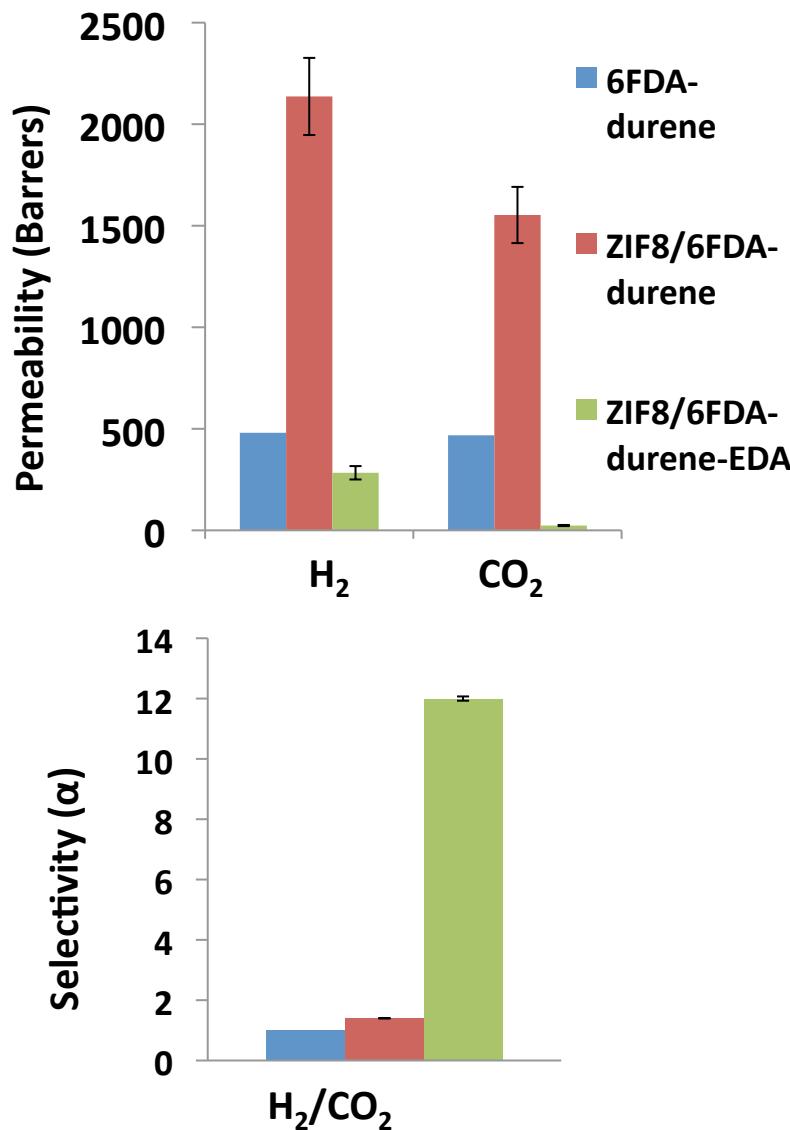
SEM image of cross-section of 50% (w/w) ZIF-8/6FDA-durene MMM before (a) and after (b) exposure to EDA for 40 min

## Asymmetric crosslinking



- Spin-coat 3 wt% solution of 6FDA-durene onto 50% (w/w) ZIF-8/6FDA-durene MMM
- Expose spin-coated 6FDA-durene skin to EDA

## ZIF-8/6FDA-Durene MMM

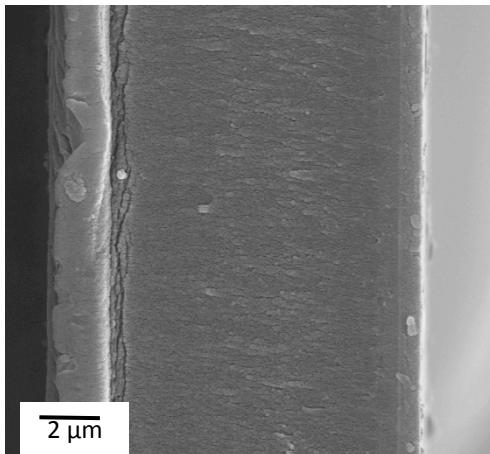


Membrane	H <sub>2</sub> (Barrers)	H <sub>2</sub> /CO <sub>2</sub>
6FDA-durene	480.4	1.0
6FDA-durene - EDA	52.1	144
ZIF-8/6FDA-durene	2137 ± 190	1.4 ± 0.0
ZIF-8/6FDA-durene-EDA	283.4 ± 33.0	12.0 ± 0.1
Asymmetric ZIF-8/6FDA-durene spin coated EDA (3 min)	505	18
6FDA-durene <sup>1</sup>	585.4	0.8
6FDA-durene - EDA <sup>2</sup>	32.6	102
ZIF-8 <sup>3</sup>	1726	4.5
Knudsen value		4.7

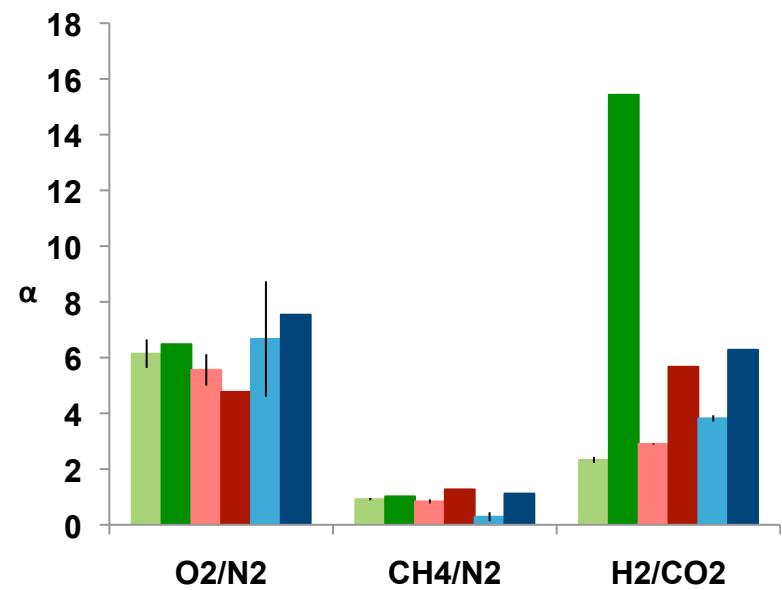
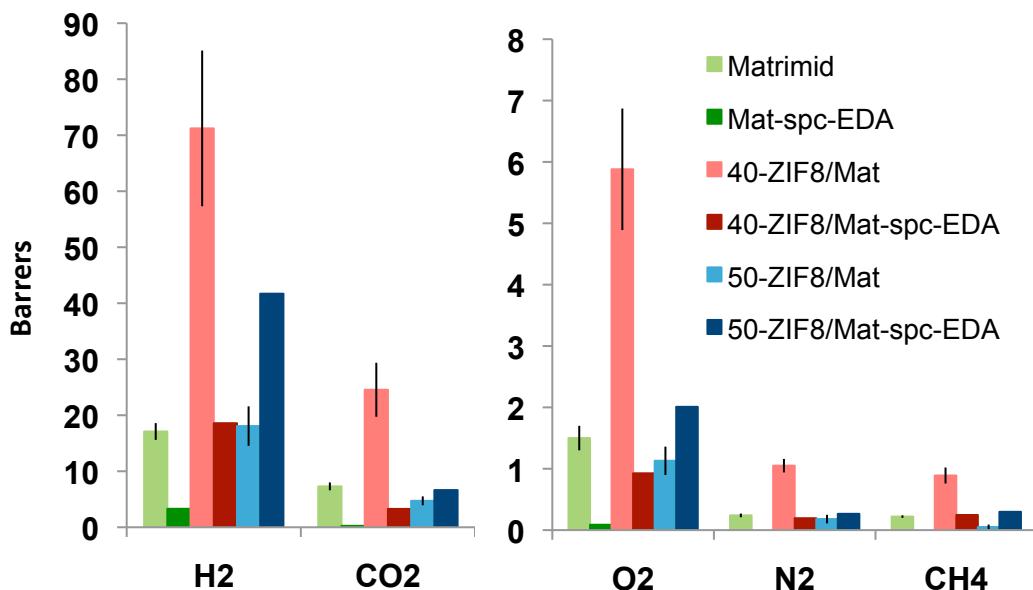
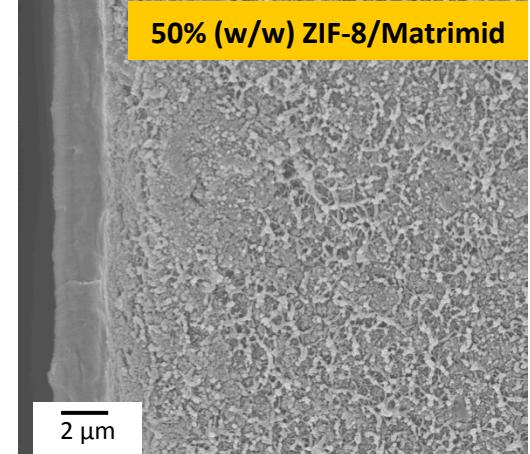
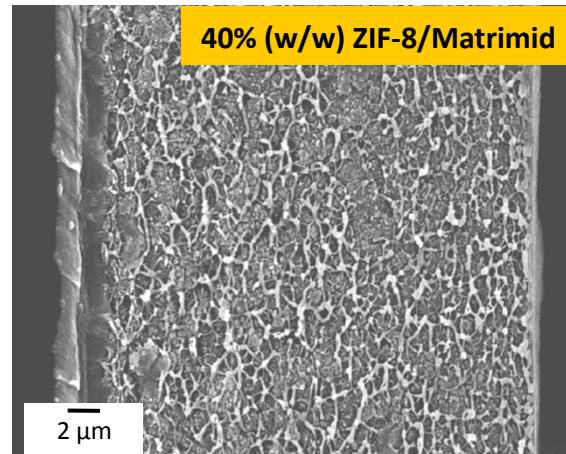
- Kanehashi, S.; Nakagawa, T.; Nagai, K.; Duthie, X.; Kentish, S.; Stevens, G. *Journal of Membrane Science* **2007**, *298*, 147-155
- Shao, L.; Lau, C.-H.; Chung, T.-S *International Journal of Hydrogen Energy* **2009**, *34*, (20), 8716-8722
- Bux, H.; Liang, F.; Li, Y.; Cravillon, J.; Wiebcke, M.; Caro, J. *J.Am.Chem.Soc.* **2009**, *131*, 16000-16001

## ZIF-8/Matrimid EDA Cross-linked MMMs

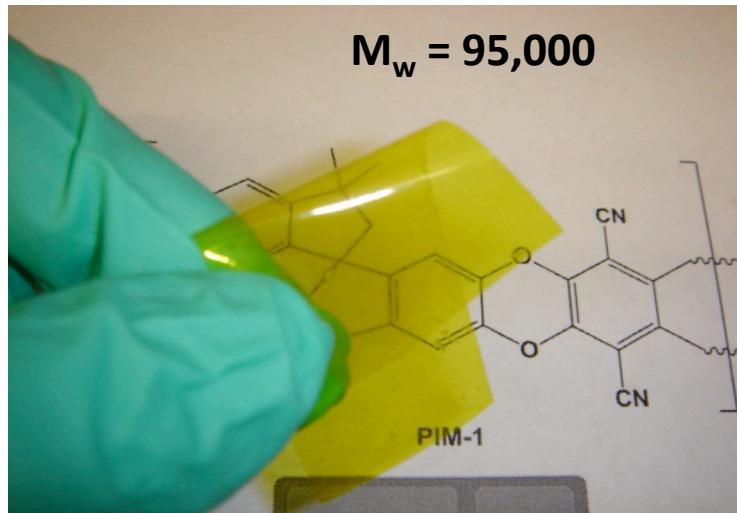
Matrimid®/EDA vapor



ZIF-8/Matrimid MMMs spin-coated with Matrimid and treated with EDA



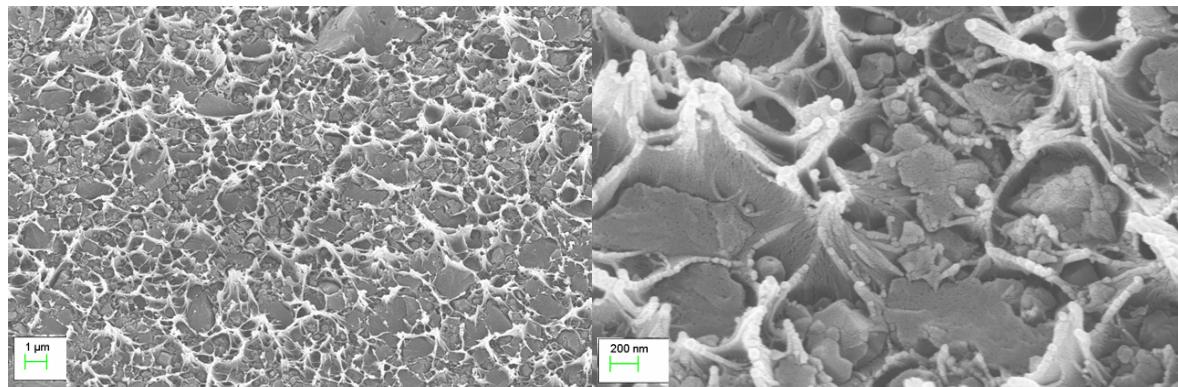
## PIM-1 Based MMMs



## PIM-1 gas separation properties

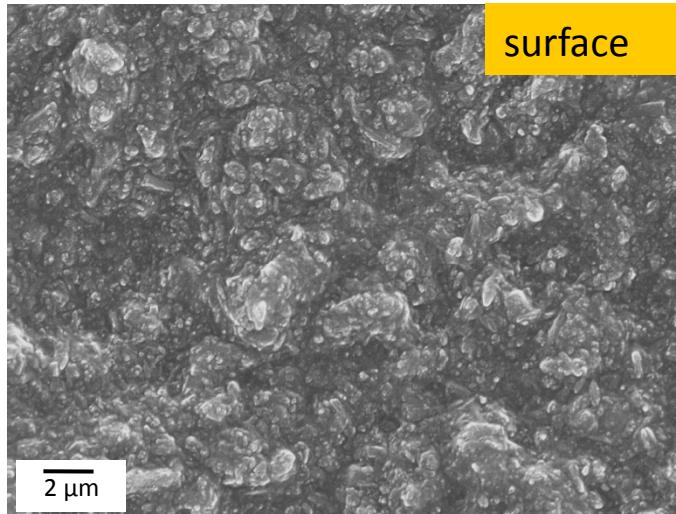
$H_2$ permeability	1509 Barrers
$CO_2$ permeability	2932 Barrers
$\alpha H_2/CO_2$	1.94

## 50% (w/w) ZIF-90/PIM-1 MMM

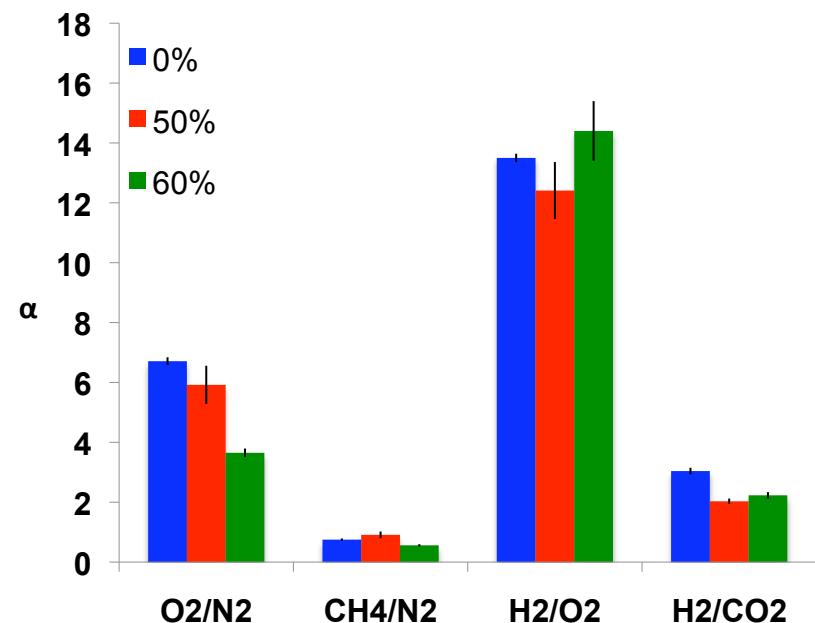
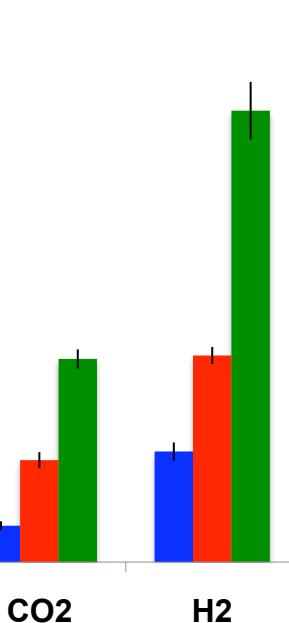
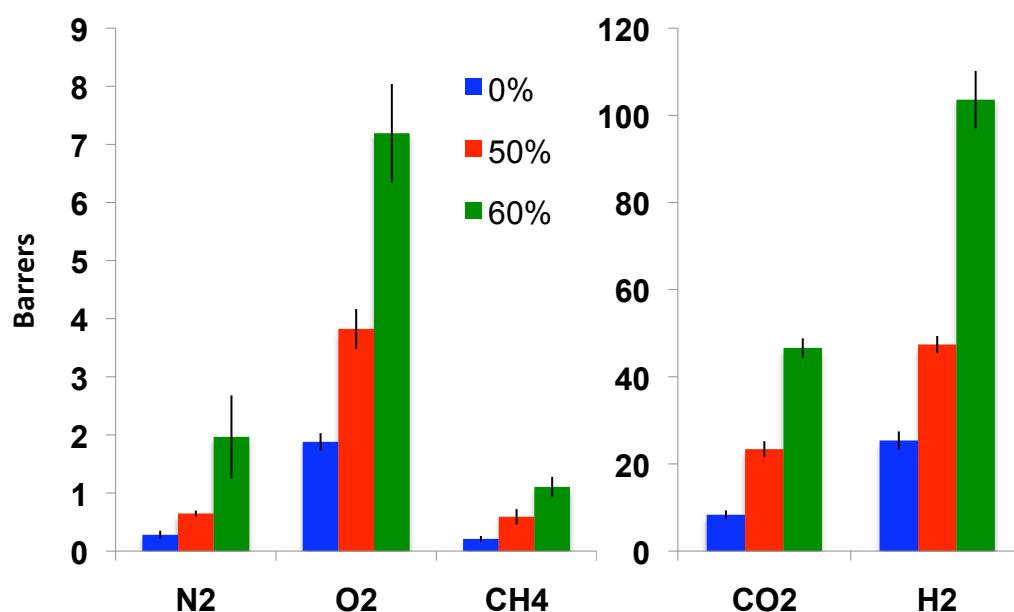
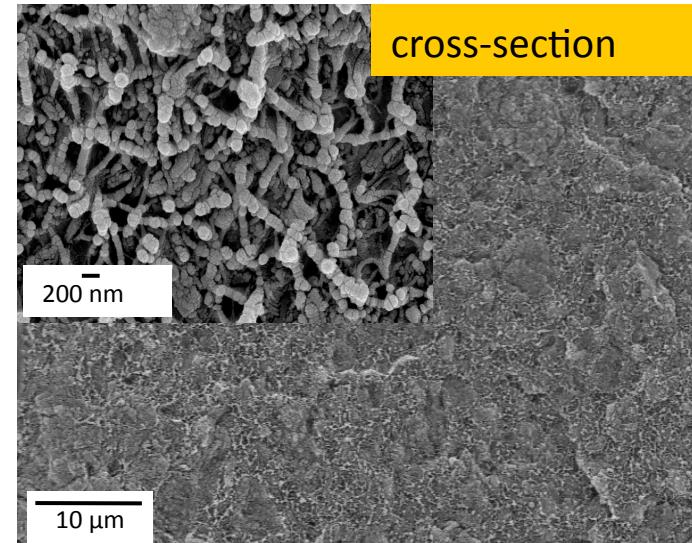


- Additives incorporated into PIM-1 form voids
- Need for functionalization of PIM-1 or ZIF-90

## MIL-53/Matrimid MMMs

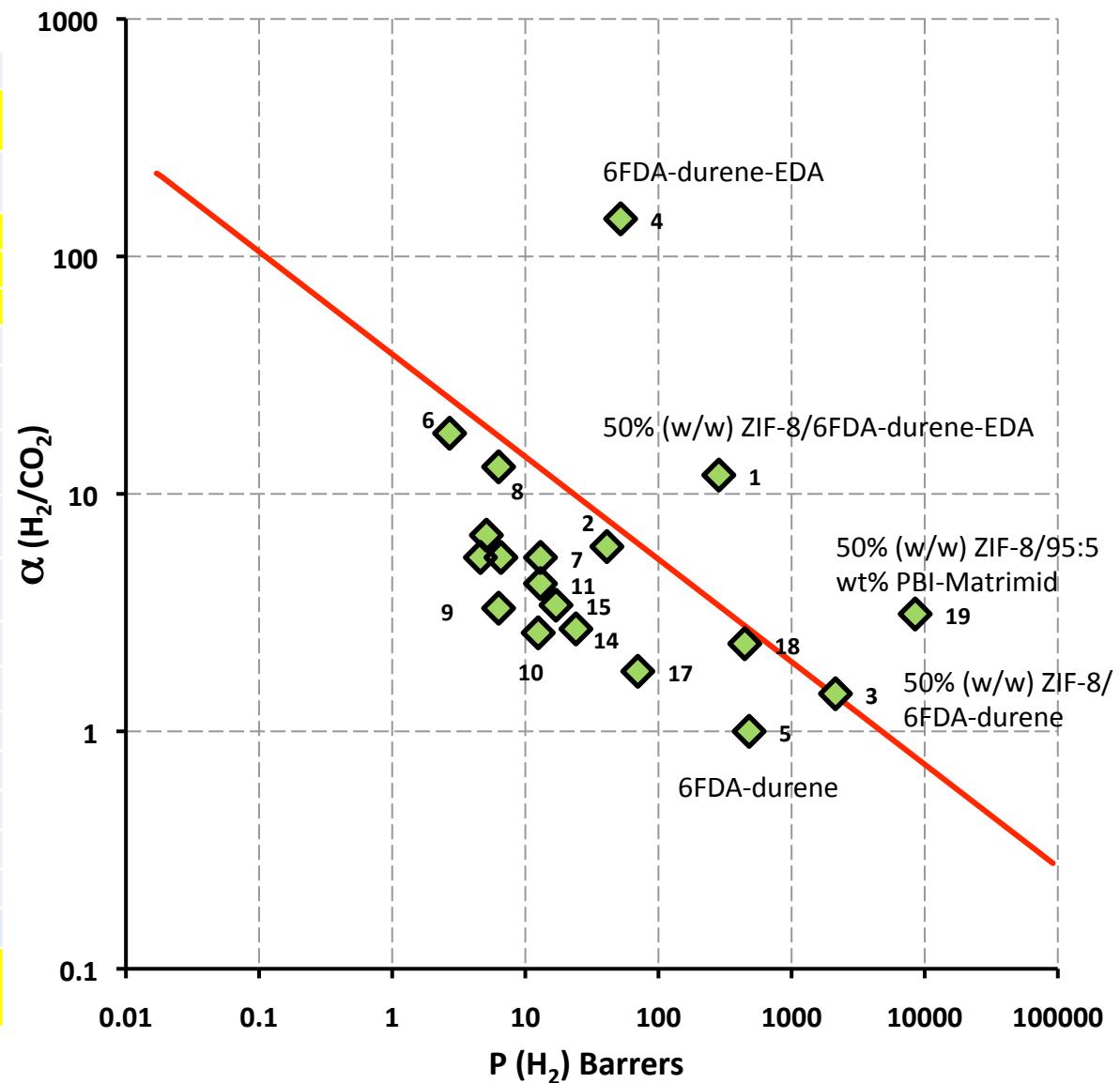


60% (w/w)  
Membrane  
dried at 200 °C  
ht framework  
(0.86 nm)



Robeson Upper Bound for H<sub>2</sub>/CO<sub>2</sub>

	PH2	H2/CO2	
50% (w/w) ZIF-8/6FDA-durene EDA MMM	284	12	1
50% (w/w) ZIF-8/Matrimid-EDA MMM	41	6	2
50% (w/w) ZIF-8/6FDA-durene MMM	2137	1.44	3
6FDA-durene-EDA	52	144	4
6FDA-durene	480	1	5
PBI (250, 35)	2.7	18	6
35% (w/w) ZIF-8/PBI MMM (180, 35)	13	5.4	7
35% (w/w) ZIF-8/PBI MMM (250, 35)	6.3	13	8
50% (w/w) ZIF-8/75:25 wt% PBI-Matrimid®	6.3	3.3	9
50% (w/w) ZIF-8/50:50 wt% PBI-Matrimid®	12.5	2.6	10
50:50% wt PBI-Matrimid®	13	4.19	11
75:25% wt PBI-Matrimid®	5.1	6.7	12
PBI	4.6	5.4	13
Matrimid	24	2.7	14
50% (w/w) ZIF-8/Matrimid	17	3.4	15
75% (w/w) ZIF-8/PBI MMM	6.56	5.4	16
6FDA-NDA	70	1.79	17
50% (w/w) ZIF-7/6FDA-NDA MMM	445	2.34	18
50% (w/w) ZIF-8/95:5 wt% PBI-Matrimid MMM	8486	3.12	19



- **Synthesized ZIFs and related frameworks and tested for H<sub>2</sub> sorption up to 350 °C and 100 atm**
- **Synthesized high performance polymers capable of withstanding high temperature environments**
- **Prepared and characterized MMMs for H<sub>2</sub> separations at 35 °C and 3 atm**
- **Constructed a high temperature-high pressure permeameter that operates at 300 °C and 30 atm**
- **Measured H<sub>2</sub> permeability in VTEC PI-1388 at 300 °C and up to 30 atm**

- Continue synthesis of ZIFs and related frameworks
- Continue synthesis of high performance polymers
- Prepare and characterize MMMs for H<sub>2</sub> separations at NETL test protocol conditions
- Continue testing membranes at DOE 2015 test conditions

## ZIF-containing MMMs offer exciting opportunities in hydrogen separations



### Postdocs

Dr. Grace Kalaw

Dr. Edson Perez

Dr. Chalita Ratanatawanate

### Graduate students

Yu (Tony) Huang

Jing Liu

Josephine Ordoñez\*

Sumudu Wijenayake

Zhen Zhang\*

### Undergraduate students

Catherine Eckert

Mishelle Kochumottom\*

Pauras Memon\*

Kelsey Musselman

William Regner

Saskia Versteeg

\*Research assistantship/summer pay from DE-NT0007636